

^{238}U -SERIES RADIONUCLIDES IN FINNISH GROUNDWATER-BASED DRINKING WATER AND EFFECTIVE DOSES

P. Vesterbacka

Radiation and Nuclear Safety Authority, STUK
University of Helsinki, Faculty of Science
Department of Chemistry, Laboratory of Radiochemistry

ACADEMIC DISSERTATION

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STUK – Radiation and Nuclear safety Authority (STUK)

P.O.Box14, FI-00881 Helsinki, Finland

Tel +358-9-759881

Fax +358-9-75988500

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Abstract

The thesis deals with the occurrence of ^{238}U -series radionuclides and particle-bound ^{210}Pb and ^{210}Po in Finnish groundwater-based drinking water, methods used for removing ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po , and the annual effective doses caused by ^{238}U -series radionuclides in drinking water. In order to reduce radiation exposure and avoid high doses, it is important to examine the activity levels of natural radionuclides in groundwater.

In this work, the activity concentrations of radon (^{222}Rn), radium (^{226}Ra), uranium (^{238}U and ^{234}U), lead (^{210}Pb) and polonium (^{210}Po) were determined from 472 private wells, which were selected randomly from across Finland. On the basis of the results, the activity concentrations in groundwater and the radiation exposure from drinking water of people living outside the public water supply in Finland was specified. The efficiency of ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po removal from drinking water was examined at ten private homes. In order to obtain accurate results and correct estimates of effective doses, attention was paid to the sampling of ^{222}Rn and ^{210}Pb , and the determination of ^{210}Po .

The results revealed that the median activity concentrations of natural radionuclides were as much as ten times higher in drilled wells than in wells dug in soil. The average activity concentration of ^{222}Rn in drilled wells was 460 Bq/l and in dug wells 50 Bq/l. The highest activity concentrations were found in Southern Finland. In addition, occasional high activity concentrations were found all over Finland. The average activity concentrations of ^{234}U and ^{238}U in drilled wells were 0.35 and 0.26 Bq/l and in dug wells 0.020 and 0.015 Bq/l, respectively. The spatial distribution of ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po was essentially similar to that of ^{222}Rn . In contrast to other natural radionuclides, the highest ^{226}Ra activity concentrations were found in coastal areas, since drilled well water near the sea has a higher salinity than water in drilled wells inland. ^{210}Pb and ^{210}Po occur in untreated groundwater as ions, molecules, complexes and bound to particles of different sizes depending on the chemical quality of the water. In Finnish groundwater, the majority of ^{210}Pb was bound to the large particle fraction. Compared to ^{210}Pb , ^{210}Po was bound more to the intermediate and small particle fraction.

Anion exchange was found to be an efficient removal method for ^{234}U and ^{238}U . In most cases, the removal efficiency was over 95%. The removal of ^{234}U and ^{238}U from drinking water reduced the annual effective dose by 0.8 mSv on average, and at maximum by 1.4 mSv. Since the removal efficiency of ^{210}Pb and ^{210}Po varies greatly, their presence in different particle-size fractions was studied. The ion exchange unit more efficiently removed ^{210}Pb and ^{210}Po bound to the small particle fraction than those radionuclides in the large particle fraction. The efficiency of activated carbon units in removing ^{210}Pb and ^{210}Po was independent of the particle size fraction.

In Finland, about 10% of the population (~500 000) permanently uses water from private wells for daily drinking and household requirements. This group receives nearly half (77.4 manSv) of the annual collective effective dose of all Finnish people due to natural radioactivity in drinking water. The average annual effective dose from natural radionuclides was estimated to be 0.4 mSv for drilled well users and 0.05 mSv for users of wells dug in soil. According to earlier studies, the maximum effective dose due to natural radioactivity in drinking water has been as high as 70 mSv. In this work, the maximum doses were 6.8 mSv for drilled well users and 0.6 mSv for users of wells dug in soil. For the users of drilled wells over 90% of the dose is caused by ^{222}Rn (75%), ^{210}Po (12%) and ^{210}Pb (5%).

An efficient way to detect high doses is to perform ^{222}Rn measurement in all drilled wells. In new houses, natural radionuclides in groundwater need to be taken into account when planning household water resources in order to avoid high costs afterwards. In connection with house planning it is also recommended to reserve adequate places for removal equipment in the utility room.

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Avainsanat Luonnon radioaktiiviset aineet, juomavesi, säteilyannos, näytteenotto, poistomenetelmät

Tiivistelmä

Väitöskirjassa tarkastellaan juomaveden ^{238}U -sarjan radionuklideja ja niistä aiheutuvaa säteilyaltistusta, ^{210}Pb :n ja ^{210}Po :n kiinnittymistä erikokoisiin pohjavedessä oleviin hiukkasiin sekä ^{234}U :n, ^{238}U :n, ^{210}Pb :n ja ^{210}Po :n poistoa juomavedestä. Tietoa tarvitaan, jotta voidaan vähentää suomalaisten juomaveden kautta saamaa säteilyaltistusta ja välttää suurimpia annoksia.

Radonin (^{222}Rn), radiumin (^{226}Ra), uraanin (^{238}U ja ^{234}U), lyijyn (^{210}Pb) ja poloniumin (^{210}Po) aktiivisuuspitoisuudet analysoitiin 472 kaivovesinäytteestä eri puolelta Suomea. Tulosten perusteella tarkennettiin arvioita suomalaisten yksityiskaivojen käyttäjien juomaveden kautta saamasta keskimääräisestä vuotuisesta efektiivisestä säteilyannoksesta. Poistomenetelmien toimivuutta selvitettiin kymmenessä yksityisessä kotitaloudessa. ^{222}Rn :n ja ^{210}Pb :n näytteenottoa sekä ^{210}Pb :n määrittämistä pohjavesinäytteistä tutkittiin, jotta varmistuttiin että valitut näytteenottotavat ja analysointimenetelmät ovat luotettavia ja antavat oikeanlaisen kuvan säteilyaltistuksesta.

Porakaivovedessä luonnon radioaktiivisten aineiden aktiivisuuspitoisuuksien mediaanit olivat mittausten mukaan jopa kymmenen kertaa suurempia kuin rengaskaivovedessä. Säteilyaltistuksen kannalta merkittävimmän nuklidin, ^{222}Rn :n, aktiivisuuspitoisuuden keskiarvo porakaivovedessä oli 460 Bq/l ja maaperän kaivovedessä 50 Bq/l. Korkeimmat pitoisuudet ovat Etelä-Suomessa, mutta yksittäisiä korkeita pitoisuuksia on kaikkialla Suomessa. ^{234}U - ja ^{238}U -aktiivisuuspitoisuuksien keskiarvot porakaivovedessä olivat 0,35 ja 0,26 Bq/l ja maaperän kaivovedessä 0,020 ja 0,015 Bq/l. Luonnon radioaktiivisista aineista ainoastaan ^{226}Ra :n esiintyminen poikkesi muiden esiintymisestä siten, että korkeat pitoisuudet löytyivät lähinnä rannikolta, kun taas muut nuklidit noudattivat pääpiirteissään ^{222}Rn :n jakautumista. Meren läheisyys rannikolla näkyy sisämaan kaivoihin verrattuna veden suurempana suolapitoisuutena, joka edistää ^{226}Ra :n liukoisuutta. ^{210}Pb ja ^{210}Po ovat pohjavedessä liukoisine yhdisteinä ja sitoutuneina erikokoisiin hiukkasiin. ^{210}Pb on suurimmaksi osaksi sitoutuneena karkeaan hiukkasaineeseen, kun taas ^{210}Po oli tasaisemmin jakautuneena kaiken kokoisissa hiukkasissa.

Ioninvaihto osoittautui tehokkaaksi menetelmäksi uraanin poistamiseksi juomavedestä. Kaikissa tutkituissa tapauksissa uraanin poistotehokkuus oli yli 95 %. Uraanin isotoopeista aiheutuvaa vuotuista efektiivistä säteilyannosta pystyttiin vähentämään vedenkäsittelyllä keskimäärin 0,8 mSv, suurimmillaan jopa 1,4 mSv. ^{210}Pb :n ja ^{210}Po :n poistotehokkuus ioninvaihtimilla ja aktiivihiili-suodattimilla on vaihdellut 0 ja 100 % välillä, minkä vuoksi niiden kiinnittymistä tutkittiin erikokoisiin pohjavedessä oleviin hiukkasiin. Ioninvaihtimilla pystyttiin poistamaan vedestä paremmin hienossa kuin karkeassa hiukkasaineuksessa oleva ^{210}Pb ja ^{210}Po . Aktiivihiili-suodattimilla ei havaittu olevan selvää vaikutusta hiukkaskoon ja ^{210}Pb - tai ^{210}Po -poistuman välillä.

Kymmenesosa suomalaisista käyttää yksityiskaivojen vettä. Tässä työssä saatujen tulosten mukaan heidän juomaveden kautta saama vuotuinen kollektiivinen efektiivinen säteilyannos (77,4 manSv) on lähes puolet kaikkien suomalaisten juomaveden kautta saamasta luonnon radioaktiivisten aineiden aiheuttamasta säteilyannoksesta. Yksittäiselle porakaivoveden käyttäjälle keskimääräinen vuotuinen efektiivinen säteilyannos on 0,4 mSv ja maaperän kaivon käyttäjälle 0,05 mSv. Aikaisempien tutkimusten mukaan juomavedestä saatava annos voi olla jopa 70 mSv. Tässä työssä korkein juomaveden kautta aiheutuva vuotuinen säteilyannos porakaivovedenkäyttäjälle oli 6,8 mSv ja maaperän kaivon käyttäjälle 0,6 mSv. Porakaivoveden käyttäjälle yli 90 % juomaveden kautta saatavasta kokonaisannoksesta aiheutuu nuklideista ^{222}Rn (75 %), ^{210}Po (12 %) ja ^{210}Pb (5 %).

Tehokkain keino korkeiden säteilyannosten löytämiseksi on ^{222}Rn -pitoisuuden mittaaminen porakaivovedestä. Uusien talojen vedenhankintaa suunniteltaessa pohjaveden luonnon radioaktiiviset aineet kannattaa ottaa huomioon, jotta jälkikäteen vältytään suurilta kustannuksilta. Talonsuunnittelun yhteydessä kannattaa myös varata sopivat tekniset tilat vedenpuhdistus-laitteille.

List of publications

This thesis consists of a scientific review (Chapters 2–7) and a study based on the following original publications referred to in the text by their Roman numbers. Additional data from ^{222}Rn sampling, quality assurance and disequilibrium of ^{238}U –series radionuclides in drilled well and dug well water is presented. Note the name change of the author from Huikuri to Vesterbacka.

- I. P. Vesterbacka, I. Mäkeläinen, H. Arvela, Natural Radioactivity in Drinking Water in Private Wells in Finland, *Radiation Protection Dosimetry* 113 (2); 223–232, 2005. Reprinted with the kind permission of Oxford University Press, Great Clarendon Street, Oxford OX2 6DP, UK.
- II. P. Vesterbacka, K. Hämäläinen and J. Lehto, The Effect of Water Treatment on the Presence of Particle-bound ^{210}Po and ^{210}Pb in Groundwater, *Radiochimica Acta* 93; 291–296, 2005. Reprinted with the kind permission of Oldenbourg Wissenschaftsverlag GmbH.
- III. P. Vesterbacka and I. Mäkeläinen. Sampling of ^{210}Pb in radon-bearing drinking water. In: Möbius S, Noakes J, Schöhofer F, Braun-Brumfiel (Eds.). LSC 2001. *Advances in Liquid Scintillation Spectrometry*. Radiocarbon, Arizona, 2002; 317–325. Reprinted with the kind permission of RADIOCARBON, Department of Geosciences, The University of Arizona, 4717 E. Ft. Lowell Road, Tucson Arizona 85712 USA.
- IV. P. Vesterbacka and T.K. Ikäheimonen, Optimization of ^{210}Pb Determination via Spontaneous Deposition of ^{210}Po on a Silver Disk. *Analytica Chimica Acta* 545; 252–261, 2005. Reprinted with the kind permission of Elsevier.
- V. P. Huikuri and L. Salonen, Removal of Uranium from Finnish Groundwaters in Domestic Use with a Strong Base Anion Resin, *Journal of Radioanalytical and Nuclear Chemistry* 245 (2); 385–393, 2000. Reprinted with the kind permission of Springer Science and Business Media.

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1. Objectives and scope

The overall objective of the work was to gather new information on the occurrence of natural radioactivity in drinking water and reduce the radiation exposure of Finnish people. In order to achieve these aims the main focus in this work was:

1. To investigate the occurrence of ^{238}U -series radionuclides in Finnish groundwater and to obtain representative estimates of the effective dose to users of private wells in Finland caused by ^{238}U -series radionuclides.
2. To examine the disequilibrium between different natural radionuclides in water in drilled wells and in water in wells dug in soil.
3. To study particle-bound ^{210}Po and ^{210}Pb in drilled well water in order to deepen our knowledge of the occurrence of these radionuclides in groundwater. Additionally, to study the effect of activated carbon and ion exchange units on particle-bound ^{210}Pb and ^{210}Po .
4. To determine the ^{238}U and ^{234}U removal efficiency of ion exchange units in private homes and the retention of ^{238}U and ^{234}U in the resin in order to be aware of restrictions connected with these units.
5. To study the sampling of ^{222}Rn and ^{210}Pb and to examine the accuracy of ^{210}Pb determination from water samples.

In publication **I** the activity concentration of ^{238}U -series radionuclides was determined from private wells in a random sampling study. A questionnaire was sent to 2,000 persons not using a public water supply as their drinking water. Of the 779 private well users who consented to participate, the wells of 472 were selected for the study. The activity concentration of ^{222}Rn and long-lived radionuclides, ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po , were determined from 288 drilled wells and 184 wells dug in soil. ^{210}Po is included among the long-lived radionuclides even though its half-life is only 138 days since ^{210}Pb continuously produces ^{210}Po in water. On the basis of the results obtained in this study, the effective doses to users of private wells were estimated.

In publication **II** the main emphasis was placed on particle-bound ^{210}Pb and ^{210}Po in order to understand their behaviour in groundwater and to better assess the removal efficiency of water treatment equipment. Publication **III** discusses the method for sampling ^{210}Pb and ^{222}Rn . Sampling, as applied to water analysis, is defined as the process of selecting a portion of material that represents the part of environment sampled. Depending on the focus of the study, water samples are collected using different sampling techniques. A good example of demanding sampling is ^{210}Pb sampling in ^{222}Rn -rich water. The main factors that need to be taken into account in sampling are discussed in publication **III**. After thoroughly

planned sampling it is essential to have good quality control for determination methods in the laboratory. Publication **IV** discusses the quality assurance and reliability issues of analytical results, especially in the determination of ^{210}Pb .

The effective dose can be restricted by removing radionuclides from drinking water in the case of a high activity concentration. An effective method for removing ^{234}U , ^{238}U and ^{226}Ra from drinking water is ion exchange, but the removal of ^{210}Pb and ^{210}Po is more challenging since they occur in groundwater bound to different-sized particles. ^{234}U and ^{238}U removal from drinking water using an ion exchange unit is discussed in publication **V** and the removal of particle-bound ^{210}Pb and ^{210}Po by use of an ion exchange and activated carbon units are discussed in publication **II**. The links between different publications in this work are presented in Figure 1.

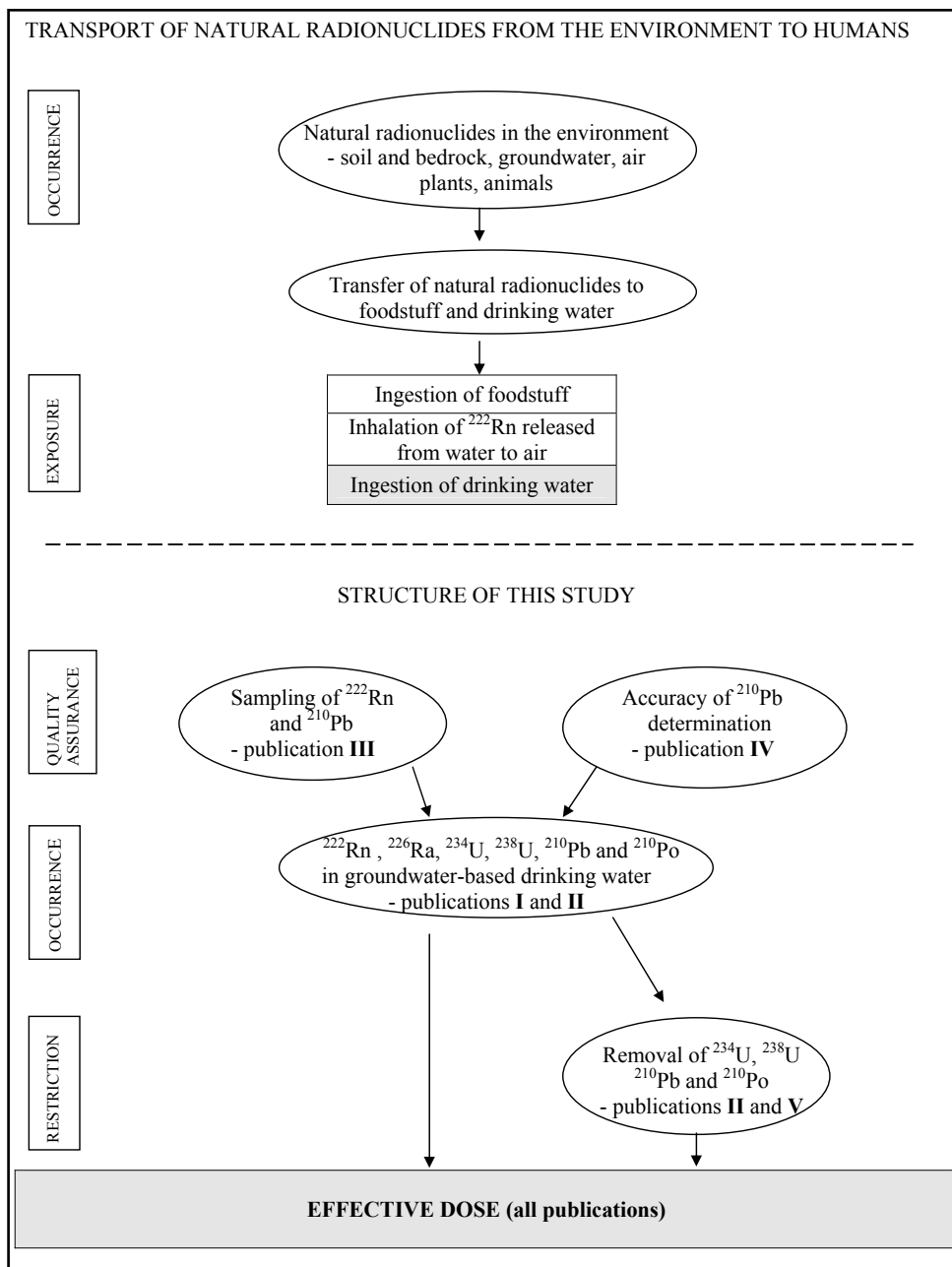


Figure 1. Transport of natural radionuclides from the environment to humans (upper figure) and links between the different publications in this study (lower figure). Roman numbers refer to the original publications (I–V).

2. Introduction

Radionuclides are naturally found throughout all environments. They are present in varying amounts in air, water, plants, animals, soil and rocks. Naturally occurring radionuclides are mainly derived from three separate decay chains (^{235}U , ^{238}U and ^{232}Th , see Appendix I). The longest-lived member is ^{232}Th , which has half-life of 1.405×10^{10} years. The immediate parent of ^{232}Th was ^{236}U , which had a life of 2.342×10^7 years and is no longer found in the environment. The second longest series is the ^{238}U -series. Naturally occurring uranium contains 99.2745% by weight ^{238}U , 0.7200% ^{235}U , and 0.0055% ^{234}U (Pfenning et al. 1998). In addition, water contains cosmogenic radionuclides (e.g. ^3H , ^7Be , ^{10}Be and ^{14}C), which are formed in the upper atmosphere, and radioactive potassium (^{40}K), whose activity concentration is a constant proportion of stable potassium.

Groundwater is formed from precipitation, which infiltrated soil and bedrock. The amount of rain and snow, evaporation, the duration of frost and the nature of soil affect the formation of groundwater. A proportion of rainwater evaporates directly and via transpiration from plants, part infiltrates soil and bedrock and part is carried along with rivers to the sea. The activity concentrations of natural radionuclides in groundwater are connected to the activity concentrations of uranium (^{238}U and ^{235}U) and thorium (^{232}Th) and their decay products in soil and bedrock. This is because groundwater reacts with soil and bedrock and releases quantities of dissolved components, depending on the mineralogical and geochemical composition of the soil and rock, chemical composition of the water, degree of weathering of the rock, redox conditions and the residence time of groundwater in the soil and bedrock.

Naturally occurring radionuclides and particularly their decay products are transported in groundwater and surface water. As a result, these radionuclides may enter the food chain through irrigation waters, and the water supply through groundwater wells and surface water streams and rivers. The health risks to humans are real, but the level of risk involved is not clearly defined. This is since we do not yet know enough about the activity concentration of these radionuclides in the environment and there have been no epidemiological studies quantifying the risk from all natural radionuclides in drinking water. The ingested ^{222}Rn exposes stomach (National Research Council 1999). In addition to the effective dose from ingested ^{222}Rn , waterborne ^{222}Rn can be a source of indoor ^{222}Rn , because during water usage ^{222}Rn is easily released from water to indoor air. Inhaled daughters of ^{222}Rn cause a dose to the lungs. Long-lived radionuclides, ^{234}U , ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po , cause a dose to the kidneys, liver, bladder, bone surface and marrow (ICRP67 1993, ICRP69 1995).

During the last 35 years, the Radiation and Nuclear Safety Authority of Finland (STUK) has studied radioactivity in drinking water that originates either from surface or groundwater sources. At the beginning the main emphasis was on radioactivity in waterworks, but subsequent research has concentrated more on private wells (Asikainen and Kahlos 1977, Asikainen 1981a, Asikainen 1981b, Asikainen 1982, Salonen 1994, Salonen and Huikuri 2002). Radioactivity has now been studied at nearly 1,000 water sources in networks or water catchments, more than 8,000 wells drilled in bedrock and 5,000 wells dug in soil in Finland. The main emphasis in these studies has been placed on identifying the risk areas in Finland and examining activity levels in different raw water sources. Therefore, less attention has been paid to the representativeness of the data.

3. Uranium and thorium in rocks and the connection between the activity concentration of ^{222}Rn in bedrock water and geology in Finland

Uranium, thorium and potassium are the major radionuclides contained in the Earth's crust (Ivanovich and Harmon 1982). Since the age of the Earth is approximately the age of ^{238}U , other radionuclides from the ^{238}U -series are also found in the crust (see Appendix I) (Lehtinen et al. 1998).

The average crystal abundance of uranium and thorium are 2.8 ppm (parts per million) and 10 ppm and the typical ranges are 1.5 – 6.5 ppm and 6 – 20 ppm, respectively (Koljonen (eds.) 1992, Plant et al. 2003). Similar levels have been observed in Finnish soil and bedrock (Arvela et al. 1979, Lemmelä 1984, Vesterbacka 1998). The average Th/U ratio in most rocks, in which uranium is not enriched, is 3.5 to 1 (Plant et al. 2003).

Uranium and thorium are incorporated into late crystallizing magmas and residual solutions due to their large ionic radii, which prevent them from existing in early crystallizing silicates. Therefore, uranium and thorium are mainly found in granites and pegmatites (Ivanovich and Harmon 1982). Typical ranges of uranium and thorium in various rock types are presented in Table 1. Rock types are classified into different groups according to how they are formed. There are three main groups: igneous, metamorphic and sedimentary rocks. Igneous rocks are formed from magma, metamorphic rocks are re-crystallized rocks and sedimentary rocks are rocks that have been formed by interpose or harden in the water or in dry land.

Finland occupies the older part of the Fennoscandian Shield (Koljonen (eds.) 1992). The primary mechanism by which the bedrock was formed includes sedimentation and melting of the mantle and the crust. About two-thirds (53%) of Finnish bedrock consists of granitic rocks and one-fifth (22%) of migmatites (Figure 2). Only a minor part of Finnish bedrock is formed from quartzite, limestone and alkaline igneous rock, schist.

Figure 2 illustrates the connection between the activity concentration of ^{222}Rn in drilled well water and the geology in Finland. The high activity concentrations of ^{222}Rn are mainly found in areas where the bedrock consists of granite. These areas are found in central and southern Finland. In the south of Finland, migmatite granites are also associated with small uranium deposits. Additionally, a large granitoid area occurs in the middle of Lapland. This area is very similar to the granitoids in central Finland, but contains a higher proportion of granites. In Lapland, greenstone is also rich in granite.

Table 1. Uranium and thorium contents in different rock types based on data from different continental and oceanic island sites (Ivanovich and Harmon 1982).

Rock type	Name	Uranium (ppm)	Thorium (ppm)
Igneous	granites, grano-diorities, rhyolites	2.2 - 6.1	8 - 33
	gabbros	0.8	3.8
	basalt	0.1 - 1	0.2 - 5
Metamorphic	granulites	4.9	21
	gneiss	2.0	5 - 27
	schist	2.5	7.5 - 19
	slate	2.7	7.5
	phyllite	1.9	5.5
Sedimentary	shales (black)	3 - 1250	-
	bauxite	11.4	49
	phosphates	50 - 300	1 - 5
	peat	1 - 12	1 - 5
	limestone	2	0 - 2.4

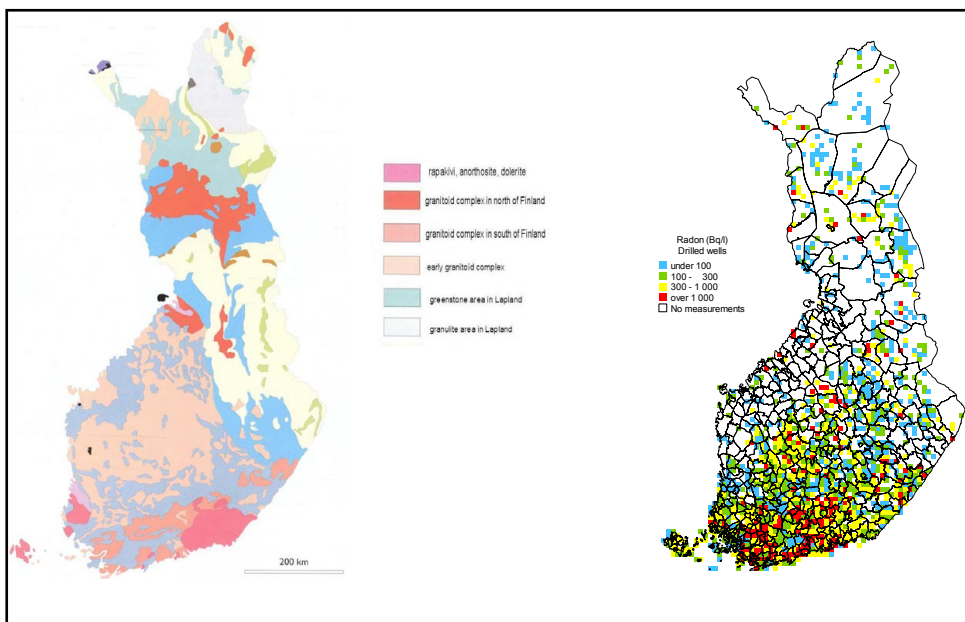


Figure 2. A simplified geological map of Finland and the distribution of ^{222}Rn (Bq/l) in bedrock water in Finland (Lehtinen et al. 1998, Voutilainen et al. 2000).

The Karelia area in the east of Finland is formed from broad stone, which comprises old sediment stones and vulcanite. There the mean activity concentration of ^{222}Rn in drilled wells is lower than in drilled wells in central and southern Finland (Voutilainen et al. 2000).

4. Geochemistry and chemistry of natural radionuclides in groundwater

4.1 ^{222}Rn

Radon is noble gas and that has three natural isotopes: ^{222}Rn , ^{220}Rn and ^{219}Rn . The most significant isotope is ^{222}Rn due to its longer half-life (3.8 days) compared to the half-lives of other isotopes of radon. In groundwater, ^{222}Rn occurs in a dissolved form and its activity concentration may vary from a few Bq/l to thousands of Bq/l. The highest activity concentrations are found from bedrock water. In surface water ^{222}Rn is generally found at very low levels (Aieta et al. 1987, Salonen 1994).

The chemical composition of groundwater does not affect the activity concentration of ^{222}Rn . The main parameters that affect the activity concentration of ^{222}Rn in groundwater are the activity concentration of ^{226}Ra in bedrock and soil, rock porosity and the ^{222}Rn emanation efficiency (Veeger and Ruderman 1998). The mobility of ^{222}Rn is mainly influenced by diffusion or by transport processes caused by the motion of gaseous or liquid phases (Juntunen 1991, Salih et al. 2004). Due to the relatively short half-life, the distance of transport of ^{222}Rn is in the range of some metres. The disequilibrium between ^{222}Rn and other uranium series radionuclides is caused by the diffusive escape of ^{222}Rn (Salih et al. 2004). Normally, the activity concentration of ^{222}Rn in groundwater is higher than the activity concentration of other uranium series nuclides (Salonen 1994).

^{222}Rn is an inert gas and does not form chemical compounds or considerably adsorb in the surrounding environment within the range of natural conditions. However, weak correlations between ^{222}Rn and other stable elements in groundwater have been observed by Salih et al. (2004). Their study showed that the fluoride ions in water, especially in low pH media, strongly affect the transport of ^{222}Rn in water. ^{222}Rn transport in water is lower at higher fluoride concentrations. Salih et al. (2004) suggested that fluoride affects the attachment of ^{222}Rn to micro-bubbles or reduces their number in water and thereby reduces the mobility of ^{222}Rn . Other studies have also found a correlation between ^{222}Rn and fluorine (Koljonen (eds.) 1992, Veeger and Ruderman 1998). The fluorine in granites is geochemically associated with the occurrence of U-bearing minerals and thus both of these elements occur in granite areas.

4.2 ^{223}Ra , ^{224}Ra , ^{226}Ra and ^{228}Ra

Radium has four natural isotopes: ^{223}Ra , ^{224}Ra , ^{226}Ra and ^{228}Ra . The activity concentration of radium in groundwater depends on the activity concentration of radium in the bedrock and on mechanisms such as precipitation-dissolution, complexation and adsorption-desorption that affect the transport of radium in water. These processes are related to the chemical composition of groundwater (IAEA 1990). In groundwater, the highest activity concentrations have been found from water containing high amounts of sodium, potassium, magnesium and calcium (saline water).

In low saline waters radium occurs as uncomplexed Ra^{2+} cations. Weak complexes with chloride, sulphate and carbonate anions are possible in saline waters, but in low saline water these have no effect on the transport of radium. The colloidal transport of radium has been less studied, but comparing it to barium it can be assumed that colloid formation could also act as a transport form for radium (IAEA 1990). Precipitation of pure radium salt is unlikely in typical Finnish groundwater. Extraordinary sulphate and radium concentrations would be required for precipitation to occur. The formation of iron and manganese hydroxides is an important mechanism for sequestering radium from groundwater. Additionally, radium may co-precipitate with barium and lead sulphates, whereas co-precipitation with CaCO_3 is minimal (IAEA 1990).

The most abundant isotopes of radium are ^{226}Ra and ^{228}Ra , which have half-lives 1600 years and 5.8 years, respectively. Of these isotopes, more information is available on ^{226}Ra than ^{228}Ra . In low saline groundwater, $^{226}\text{Ra}/^{228}\text{Ra}$ ratios have varied over a very wide range. In the literature, values from 0.07 to 41 have been reported. There have been fewer reported results from saline than low saline waters. Reported $^{226}\text{Ra}/^{228}\text{Ra}$ ratios have varied from 0.44 to 4, which is clearly lower than $^{226}\text{Ra}/^{228}\text{Ra}$ ratio in low saline water (IAEA 1990). In most studies, the $^{226}\text{Ra}/^{228}\text{Ra}$ ratio has been higher at greater activity concentrations of ^{226}Ra and ^{228}Ra (IAEA 1990). The activity concentration of ^{224}Ra and ^{223}Ra has been studied to a notably lesser extent than the activity concentration of ^{226}Ra and ^{228}Ra (IAEA 1990).

In Finnish groundwater, the activity concentration of ^{226}Ra is unrelated to that of dissolved uranium (Salonen 1994, Salonen and Huikuri 2002). There has obviously been a closer relation to the groundwater chemistry than to the radium content of the host rock. Correlations between ^{226}Ra and chlorine, bromide, iodide, sulphate, calcium, inactive strontium, sodium and lithium have been found (Tarvainen et al. 2001). These elements are typically found in saline water.

4.3 ^{234}U , ^{235}U and ^{238}U

Uranium is a member of the actinide group. The predominant forms of uranium in natural waters are ^{234}U and ^{238}U . As a result of its low abundance in the earth's crust, ^{235}U typically occurs in low concentrations in natural waters (Aietä et al 1987). Uranium can exist in four different oxidation states, namely +III, +IV, +V and +VI, but in natural waters it is generally present in the +IV or +VI state. The activity concentration of uranium in groundwater depends on its activity concentration in the bedrock and soil, the proximity of uranium-rich rocks and water, the pH and oxidation state of uranium, and the concentration of carbonate, fluoride, phosphate and other species in the water that can form uranium complexes or insoluble minerals. The presence of highly sorptive materials such as organic matter and iron and manganese hydroxides affects the activity concentration of uranium in groundwater (Langmuir 1978).

In environments that are O_2 deficient and in which the pH is less than 7, uranium is more stable in the +IV oxidation state (uranous U^{4+}) than in the +VI oxidation state (uranyl UO_2^{2+}). Under oxidizing conditions, uranous species are oxidized to uranyl species (Durrance 1986, Langmuir 1978).

Uranium is chemically immobile in the +IV oxidation state. This is because it tends to precipitate in a wide range of natural conditions. The mobility of uranium is enhanced by orders of magnitude when it is oxidized to its hexavalent state. This is because uranyl species are more soluble than uranous species. Additionally, uranyl complexes in the range of natural conditions are more stable than uranous complexes (Langmuir 1978).

The solubility of uranium also depends on the mineralogical location of uranium in the rock. When uranium is held in minerals like uraninite (UO_2) or calcite (CaCO_3), in suitable circumstances it may move from the rock to groundwater. For example, under reducible conditions (oxidation potential, $\text{Eh} < 0$) uraninite is extremely insoluble. However, when the Eh is intermediate ($\text{Eh} \sim 0\text{--}0.2\text{V}$), the oxidation and leaching of uraninite is greatly enhanced when carbonate is present to form highly stable uranyl complexes (Hostetler and Garrels 1962, Langmuir 1978).

In groundwater, uranium is usually complexed (Langmuir 1978). However, it requires suitable Eh – pH conditions, in which UO_2^{2+} ions are stable and form complexes (Figure 3). The dominant species depends on the oxidation potential (Eh) and hydrogen ion activity (pH), the activity concentration of uranium, the availability of complexing ions and temperature. The mean pH values in bedrock water and in water in dug wells in Finland are 7.1 and 6.5, respectively (Tarvainen et al. 2001). The oxidation (redox) potential of groundwater is affected by the levels of oxygen, iron, manganese, nitrogen, sulphur and organic matter. Conditions in Finnish groundwater used as household water are typically oxidizing (positive Eh

value), since the percentage saturation of oxygen in groundwater is on average 40–60% (Tarvainen et al. 2001). Figure 3 shows that under such circumstances, also taking into account the pH in groundwater, the main uranium species are UO_2CO_3 and $\text{UO}_2(\text{CO}_3)_2^{2-}$.

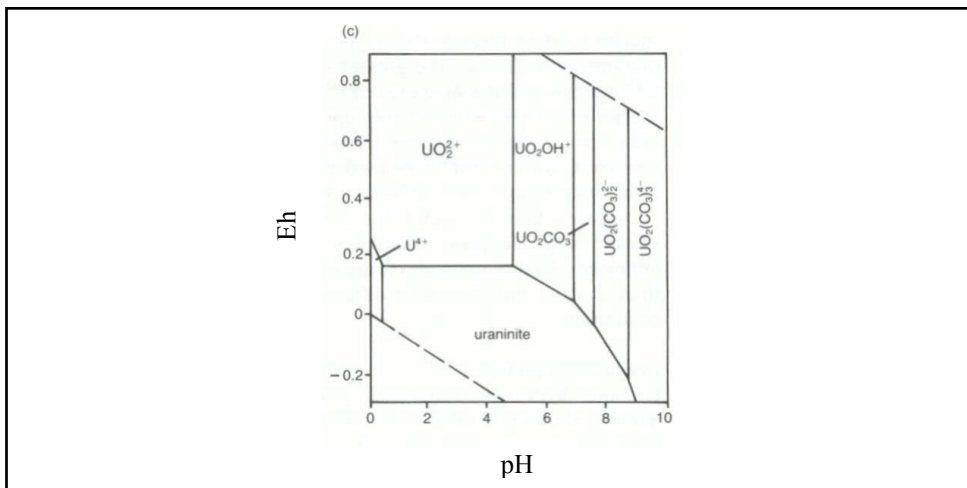


Figure 3. Eh–pH diagram for different uranium species. The partial pressure of CO_2 is $10^{1.5}$ Pa, temperature 25°C and total dissolved uranium $\text{U} = 10^{-8}\text{M}$, equivalent to a ^{238}U concentration of $2.4\text{ }\mu\text{g/l}$ (Durrance 1986).

Figure 4 illustrates the distribution of the uranyl-hydroxy, uranyl carbonate and uranyl complexes in the presence of F, Cl, SO_4 , PO_4 and SiO_2 . Figure 4(a) shows that when uranium is the only species in groundwater, free uranyl ions are the main species below pH 5. At pH values higher than 5, hydroxy complexes start to dominate. Hydroxy complexes are not the predominant species when other complexing elements are present. The dominant complexing element for uranium is CO_3^{2-} . Figure 4(b) shows the different carbonate complexes in relation to pH. The most stable carbonate complex is $\text{UO}_2(\text{CO}_3)_2^{2-}$ over the pH range from 6.5 to 8, which is a typical range of pH in Finnish groundwater. Figure 4(c) illustrates that when other complexing elements, like F, Cl, SO_4 , PO_4 and SiO_2 , are present in groundwater these may also form complexes with uranyl ions. Of these the main uranyl complexes are fluoride between pH 3 to 4, phosphate between pH 4 to 7.5 and the carbonate complexes above pH 7.5. The importance of F, Cl, SO_4 and SiO_2 complexes is minor, since these are predominant species only in acidic conditions. The complexes with PO_4 are significant at up to pH 8.

The importance of organic substances in complexing with uranium is known. The most important natural ligands are humic and fulvic acids. These acids solute, transport and reprecipitate uranium in natural waters (Crancon

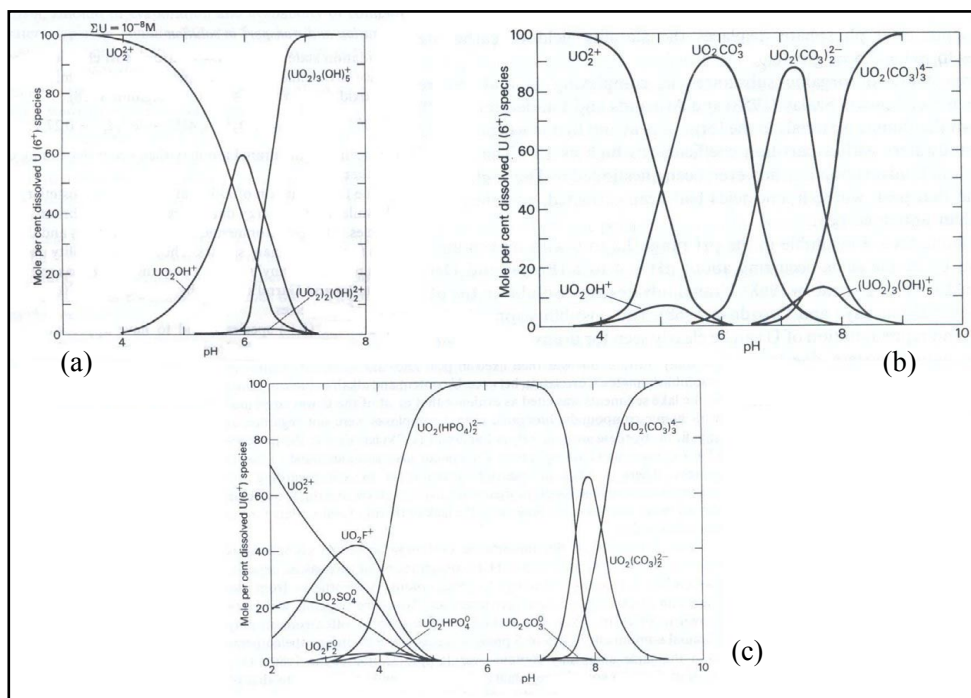


Figure 4. Distribution of uranium-hydroxy complexes (a) and carbonate complexes (b) in relation to pH at a uranium concentration of 2.4 µg/l (10^{-8} M) and at 25 °C. The bottom figure (c) presents uranyl complexes in the presence of F (0.3 mg/l), Cl (10 mg/l), SO_4 (100 mg/l), PO_4 (0.1 mg/l) and SiO_2 (30 mg/l) (Ivanovich and Harmon 1982).

and Lee 2003, Ivanovich and Harmon 1982). Formation of uranium complexes is pH dependent, since the degree of ionization of humic and a fulvic acid varies according to the pH (Silva and Nitsche 1995). Generally, organic substances play an important role in uranium adsorption under acidic conditions (Crancon and Lee 2003, Silva and Nitsche 1995). At a neutral pH, carbonate complexes are the prevailing complexes.

4.4 ^{210}Pb

Lead has both stable and radioactive isotopes. The stable isotopes are ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb , of which ^{206}Pb , ^{207}Pb and ^{208}Pb are the end products of the decay series of ^{238}U , ^{235}U and ^{232}Th , respectively. The radioactive isotopes of the decay series are ^{210}Pb , ^{211}Pb , ^{212}Pb and ^{214}Pb , of which the longest lived is ^{210}Pb with a half-life of 22.3 years. Pb exists at oxidation states of +II and +IV. In aqueous solutions it is found in the +II state. In groundwater, Pb is found in an inorganic form, complexed with organic matter and adsorbed onto particles.

In acid groundwater, at a pH less than 6, Pb exists as an ionic form. In the pH range from 6 – 12 it is hydrolyzed and appears mainly in the form of $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2$, but also in form of $\text{Pb}_3(\text{OH})_4^{2+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$ (Ulrich and Degueldre 1993). These hydrolyzed products easily form compounds with other elements in groundwater. Thus, in groundwater, Pb is often bound in inorganic and organic colloids (Lehto et al. 1999, Lieser and Ament 1993a, Lieser and Ament 1993b, Vaaramaa et al. 2003). Pb may form also weakly soluble compounds such as PbCO_3 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, PbSi_2O_3 , $\text{Pb}_2\text{Si}_2\text{O}_7$, PbS and PbSO_4 (Lieser and Ament 1993a).

In saline water, Pb may exist as a chlorine complex, namely $\text{PbCl}_2(\text{aq})$, PbCl^+ or PbCl_3^- (Zukin et al. 1987). These are soluble within a rather large pH range. Pb may also form compounds with organic matter, which are mobile in groundwater (Lieser and Ament 1993a).

4.5 ^{210}Po

Polonium only has radioactive isotopes. Seven of these isotopes occur in the natural decay series: ^{210}Po , ^{211}Po , ^{212}Po , ^{214}Po , ^{215}Po , ^{216}Po , and ^{218}Po . Of these isotopes, the most important is ^{210}Po , which has a half-life of 138 days. Polonium may exist in the oxidation states of –II, +II, +IV and +VI. Of these, the +IV state is the most stable in solution. Polonium easily forms complexes and adsorbs onto different surfaces in the environment (Figgins 1961).

In strongly acidic conditions, polonium occurs as Po^{4+} . It may also form complexes with oxalic acid and phosphorus acid. In weakly acidic and neutral groundwater, polonium appears as $\text{PoO}(\text{OH})^+$, $\text{PoO}(\text{OH})_2$ and PoO_2 , whereas in alkaline conditions the predominant form is PoO_3^{2-} . In the hydroxyl form ($\text{PoO}(\text{OH})_2$), ^{210}Po is easily adsorbed onto inorganic and organic colloids of different sizes (Ulrich and Degueldre, 1993). In groundwater, the activity concentration of ^{210}Po is so low that the formation of intrinsic colloids is unlikely.

4.6 Disequilibrium of radioactivity in groundwater

^{238}U and ^{232}Th maintain the radioactivity of their decay series in rock, soil and ground. The activity concentration of each radionuclide is controlled by radioactive decay and chemical and other physical processes. Due to these processes, radionuclides either leave or enter groundwater, causing disequilibrium with the nuclides in the decay series (Figure 5). Some daughter nuclides of uranium and thorium are too short-lived to become fractionated from their previous parents. An example is ^{222}Rn and its short-lived daughters. If diffusion of ^{222}Rn is negligible, ^{210}Pb is likely to be in equilibrium with its progenitor ^{226}Ra . A radioactive secular

equilibrium is attained if the system is not interfered with. In equilibrium, the activity concentration of daughter nuclides is equal to the activity concentration of their respective parent and the activity concentration decreases according to the half-life of the parent nuclide (Ivanovich and Harmon 1982).

Bedrock and soil interact with groundwater. During the interaction, radionuclides may transfer from bedrock and soil to groundwater by dissolution, desorption, erosion or atomic recoil by radioactive decay (von Gunten and Benes 1995). In groundwater, elemental and isotopic disequilibrium exists both within and between uranium- and thorium-series nuclides. The disequilibrium is the greatest in deep groundwaters, such as in drilled well water (Salonen and Huikuri 2002). The most significant reason for disequilibrium in groundwater is the different chemical and physical properties of each nuclide, which affect the ability of nuclides to dissolve and move in water. The chemical properties of a nuclide influence its dissolution, adsorption, desorption, precipitation and sedimentation. Examples of physical properties that differ between nuclides are the diffusion coefficient and half-life.

^{234}U and ^{238}U are an example of isotopic disequilibrium. In unweathered minerals, the activity concentration of ^{234}U and ^{238}U isotopes is equal (Durrance 1986, Ivanovich and Harmon 1982). However, in groundwater ^{234}U nearly always has a higher activity concentration than ^{238}U . The mean isotopic ratio ($^{234}\text{U}/^{238}\text{U}$) in Finnish bedrock water has been 2 and the range is between 1 – 3 at the 95% confidence level (Salonen and Huikuri 2002). The highest $^{234}\text{U}/^{238}\text{U}$ ratio measured in Finnish bedrock water has been 11 (database of STUK, 2005). Higher activity ratios are often associated with lower activity concentrations of ^{234}U and ^{238}U . In the literature, $^{234}\text{U}/^{238}\text{U}$ activity ratios of up to 30 have been reported in groundwater (Ivanovich and Harmon 1982).

Three main factors enhance the mobility of the ^{234}U isotope: alpha recoil, changes in the crystal lattice due to recoil displacement or oxidation and chemical fractionation of ^{234}Th (Suksi 2001). ^{238}U decays via ^{234}Th and $^{234\text{m}}\text{Pa}$ to ^{234}U . When ^{238}U decays by alpha emission, the released daughter nuclide (^{234}Th) receives kinetic energy via alpha recoil. Due to alpha recoil, ^{234}Th is transferred in the crystal 20 – 50 nm, causing changes in the crystal lattice. If ^{234}Th is born near the water-rock interface it may transfer directly to the groundwater. Otherwise, alpha recoil enhances the mobility of ^{234}Th in the crystal lattice and therefore also the mobility of $^{234\text{m}}\text{Pa}$ and ^{234}U . ^{234}Th and $^{234\text{m}}\text{Pa}$ are less soluble and shorter lived than ^{234}U , and therefore the effect of alpha recoil is not observed in activity concentrations of ^{234}Th and $^{234\text{m}}\text{Pa}$ so much.

In igneous rock, uranium typically occurs in the +IV oxidation state, but may become oxidized to the +VI state, which is an order of magnitude more soluble than uranium in the +IV oxidation state (Durrance 1986). Due to alpha

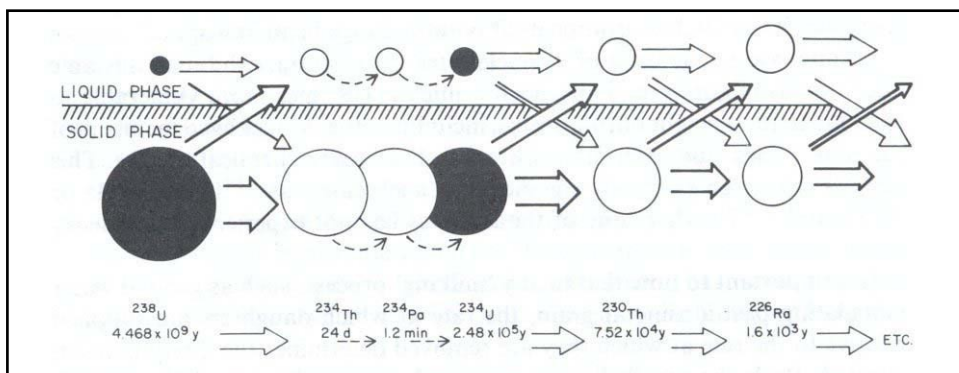


Figure 5. The recoil model of disequilibrium of ^{238}U -series nuclides. As minerals usually have a higher uranium content than water, the transfer of daughter nuclides from the solid to liquid phase is the typical direction of movement (Durrance 1986, Ivanovich and Harmon 1982).

recoil, ^{234}Th may collide to oxygen atoms in oxygen-rich minerals and generate oxygen radicals. In addition, as a big atom, ^{234}Th may pile up oxygen atoms, when ^{234}U is born in oxygen-rich conditions and becomes oxidized. The chemical fractionation of ^{234}Th is not an important mechanism taking into account ^{234}Th geochemistry (Suksi 2001).

4.7 Particles and colloids in groundwater

The transport of radionuclides in groundwater depends to a large extent on the transport of particles and colloids, since particles and colloids adsorb radionuclides. Groundwater contains ions, molecules, complexes and particles of different sizes. Particles with size between 1–450 nm are often called colloids, although the size of colloids cannot be exactly defined. However, colloids are well dispersed particles, which have a very low settling velocity (Degueldre et al. 2000). The colloids in natural groundwater consist mainly of fine clay particles, silica, iron and manganese hydroxides, humic and fulvic acids. Near the surface, increasing amounts of colloidal humic substances are found (Lieser et al. 1990). Colloids are continuously changing particles; they are continuously generated, undergo compositional changes and are removed from water. Smaller particles form aggregates and larger particles settle onto the bottom sediments. The aggregation of particles is termed coagulation (Stumm and Morgan 1996). Particles of different sizes coagulate at various rates. Initially, small particles coagulate rapidly, particles with an intermediate initial size coagulate slowly and large particles are mainly affected by sedimentation.

Colloids containing radionuclides can be divided into two separate groups. The first group consists of carrier colloids, in which radionuclides are adsorbed or co-precipitated onto colloids formed by other elements. Carrier colloids include Fe, Mn and other metal hydroxides and oxides and humic and fulvic acids. The second group are intrinsic colloids, which are particles formed by a radionuclide element. The mass concentration of radionuclides is often so small that formation of intrinsic colloids is not possible, since the solubility constant is not exceeded (Lieser et al. 1990, Silva and Nitsche 1995).

4.8 Activity concentration of natural radionuclides in different countries

Activity concentration of natural radionuclides in groundwater has been studied worldwide and the results are summarised in Table 2. The results are not comparable, since only restricted areas in various countries have been studied. However, an impression of the level of activity concentrations of natural radionuclides in groundwater in various countries can be obtained.

In Finland, activity concentrations of ^{238}U -series radionuclides in groundwater have been examined since 1970. A summary of all results is presented in Table 2. Since the sample collection was not representative, reported mean values are weighted according to the geographical frequencies of wells in each municipality. The numbers of drilled wells was obtained from a representative indoor radon study and numbers of both well types from a national rural well survey conducted by the Finnish Environment Institute (Mäkeläinen et al. 2002). However, this did not necessarily fully correct for the lack of representativeness, since water samples were not representatively collected inside the municipality. More measurements were available from areas where high activity concentrations were detected. Therefore, the mean activity concentrations reported in Table 2 are higher than attained in this study.

The highest activity concentrations of natural radionuclides have been reported from Finland. In Finland, Sweden, Norway and Ukraine, natural radioactivity in groundwater has been found to be very similar. The overall radionuclide activity concentration is dominated by that of ^{222}Rn . The mean activity concentration of ^{226}Ra was higher ($>0.15\text{ Bq/l}$) in Sweden, Ukraine, Germany and Spain compared to results obtained from China, France and Brazil. Reasons for differences in activity concentrations are the differing chemical composition of water between countries and the differing activity concentration of uranium and thorium in soil and bedrock. In central Europe, the mean ^{238}U concentration was typically low, less than $10\text{ }\mu\text{g/l}$. Higher mean concentrations than $20\text{ }\mu\text{g/l}$ were found in Finland, Sweden, Norway, Ukraine and Spain.

Additionally, in France the mean ^{238}U concentration was elevated compared to mean concentrations in Slovenia, Germany, Brazil and China. Studies including determinations of ^{210}Po and ^{210}Pb in European counties are scarce compared to those examining ^{222}Rn , ^{238}U and ^{226}Ra .

The radionuclide activity concentrations in groundwater in Finland, Sweden and Norway and the distribution of crystalline rocks dominated by granitoids in Scandinavian indicated that there is a lithological dependence between natural radioactivity in groundwater and in bedrock and soil (Isam Salih et al. 2002, Midtgård et al. 1998, Salonen 1994, Strand et al. 1998, Voutilainen et al. 2000). High activity concentrations of natural radionuclides in groundwater in other European countries were found from Spain, Germany, France and Ukraine (Fernandez et al. 1992, Gans et al. 1987, Saumande et al. 1973, Zelensky et al. 1993). Crystalline complexes also occur in some areas of these countries in Europe.

Crystalline areas are also found in other parts of Europe, namely from western *Czech Republic*, northern *Austria*, the southern *Balkans*, the Central *Alps*, *Corsica* and *Sardinia* and the *Scottish Highlands*. Additionally, there are smaller areas where uranium deposition can be found. Increased activity concentrations of natural radionuclides may be found in groundwater in these countries.

In the United States, the activity concentration of ^{222}Rn , ^{226}Ra and uranium in groundwater has been extensively studied. There, high concentrations are also attributed to uranium minerals in granite and uranium minerals in pegmatite associated with metamorphic rocks (Aieta et al. 1987, Dixon and Lee 1988, Zapecza and Szabo 1986).

^{222}Rn in groundwater is most prevalent in the north-eastern United States, especially in the New England area. High activity concentrations have been reported from Maine, Connecticut, New Hampshire and Pennsylvania (Vitz 1989, Zapecza and Szabo 1986).

The modal activity concentration of ^{234}U and ^{238}U in groundwater is between 0.07–0.19 Bq/l (Aieta et al. 1987). The highest average activity concentrations of uranium are in the western United States from Colorado, Wyoming, New Mexico, Arizona, Utah, Oklahoma, South Dakota Nebraska and Kansas (Zapecza and Szabo 1986).

^{226}Ra , at activity concentrations greater than 0.19 Bq/l, has been found in the south-eastern and the northern-central States. The south-eastern states are Georgia, North Carolina, South Carolina and Virginia. The northern-central States are southern Minnesota, southern and eastern Wisconsin, northern Illinois, Iowa and Missouri (Zapecza and Szabo 1986).

^{210}Pb and ^{210}Po is typically found in groundwater at very low activity concentrations (Aieta 1987). Elevated concentrations have been reported in uranium deposits. Additionally, in west central Florida, exceptionally high activity concentrations of ^{210}Po , up to 92 Bq/l, have been found in shallow wells (Burnett et al. 1987).

Table 2. Summarized data on concentrations of natural radionuclides in groundwater from various countries. D = drilled well, G = groundwater (dug wells and springs), T = tap water, DW = Drinking water, M = mineral water.

Nuclide	Country	Water source	Number of samples	Mean	Maximum	Reference
²²² Rn (Bq/l)	Finland	D	7000	590	77 500	Salonen and Huikuri 2002,
		G	5000	60	4 400	Mäkeläinen et al. 2002
	Sweden	D	328	257	8 105	Isam Salih et al. 2002
	Norway	D	3494	390	32 000	Strand et al. 1998
		D	1600	700 ⁽⁴⁾	19 900	Midtgård et al. 1998
	Denmark	D	68	140	1 070	Ulbak and Klinder, 1984
	Ukraine	D	1536	102	2 661	Zelensky et al. 1993
	New Zealand	D	22	28	42	Gregory 1976
	Switzerland	DW	360	6 ⁽⁵⁾	380 ⁽⁵⁾	Deflorin et al. 2004
	Spain	D	32	600	25 000	Soto et al. 1988
		G	305	98	1 200	Galan Lopez et at. 2004
	Germany	G + D	94	111	1 165	Gans et al. 1987
	China	G + D	282	229	3 735	Zhuo et al. 2001
	Brazil	G + D	88	-	75	Almeida et al. 2004
	France	G + D	54	296	3 330	Saumande et al. 1973
	Slovenia	G	500	1	75	Kobal et al. 1990
	Scotland	G	70	23 – 61	76	Al-Doorie et al. 1993
	Greece	G	12	-	13	Kritidis and Angelou 1984
	United Kingdom	T + G	512	3.5	220	Henshaw et al. 1993
	Pennsylvania (USA)	G + D	661	124	3 800	Vitz 1989, Cech et al. 1988
	Texas (USA)	G + D	11	9	122	Vitz 1989, Cech et al. 1988
	Florida (USA)	G + D	10	8	15	Vitz 1989
	Connecticut (USA)	G + D	469	400	14 000	Vitz 1989
	New Hampshire (USA)	G + D	165	340	4 000	Vitz 1989
	Colorado (USA)	G + D	33	173	11 000	Vitz 1989
	Maine (USA)	G + D	154	155	59 200	Lowry et al. 1987, Cech et al. 1988
²²⁸ Ra (Bq/l)	Switzerland	DW	360	-	0.06 ⁽⁵⁾	Deflorin et al. 2004
	Switzerland	M	42	0.03 ⁽⁵⁾	0.4 ⁽⁵⁾	Deflorin et al. 2004
	Germany	G + D	12	0.02	0.04	Gans et al. 1987
	China	G + D	137	0.047	0.49	Zhuo et al. 2001
	Brazil	G + D	88	0.26 ⁽⁴⁾	1.5	Almeida et al. 2004
²²⁶ Ra (Bq/l)	Finland	D	2700	0.06	49	Salonen and Huikuri 2002,
		G	2200	0.01	2.0	Mäkeläinen et al. 2002
	Sweden	D	328	0.26 ⁽³⁾	4.9	Isam Salih et al. 2002
	Denmark	D	79	-	0.55	Ulbak and Klinder, 1984
	Ukraine	D	520	0.38	5.2	Zelensky et al. 1993
	Switzerland	DW	360	< 0.02 ⁽⁵⁾	1.5	Deflorin et al. 2004, UNSCEAR 2000
	Switzerland	M	42	0.035 ⁽⁵⁾	0.13 ⁽⁵⁾	Deflorin et al. 2004
	Spain	D	345 ⁽¹⁾	0.84	9.26	Fernandez et al. 1992
		G	345 ⁽¹⁾	0.025	0.07	
		D	32	1.0	4.0	
	Germany	G + D	192	0.15	6.29	Soto et al. 1988
	China	G + D	428	0.03	0.94	Gans et al. 1987
	Brazil	G + D	88 ⁽¹⁾	0.02 ⁽⁴⁾	0.49	Zhuo et al. 2001
	Brazil	G	268	0.078	3.4	Almeida et al. 2004
						IAEA 1984

Table 2 continues

Nuclide	Country	Water source	Number of samples	Mean	Maximum	Reference
²²⁶ Ra (Bq/l)	France	G + D	54	0.08	0.53	Saumande et al. 1973
	Slovenia	G	500	0.02	0.51	Kobal et al. 1990
	United Kingdom	DW	-	-	0.18	UNSCEAR 2000
	Poland	D	6	0.104	0.33	Grzybowska et al. 1983
	Poland	G	16	0.012	0.029	Grzybowska et al. 1983
	Italy	DW	-	-	1.2	UNSCEAR 2000
	Maine (USA)	D	33	2.4	27	Smith et al. 1961
	New Hampshire (USA)	D	12	0.26	0.85	Smith et al. 1961
	Florida (USA)	G	246	0.098	2.8	IAEA 1984
	Texas (USA)	G	24	0.68	6.3	IAEA 1984
²³⁸ U (µg/l)	Finland	D	7000	32	20 000	Salonen and Huikuri 2002, Juntunen
		G	5000	1.6	89	1991, Mäkeläinen et al. 2002
	Sweden	D	328	14.3 ⁽³⁾	427	Isam Salih et al. 2002
		D	476	34 ⁽⁴⁾	750	Midtgård et al. 1998
	Norway	D	150	6 ⁽⁵⁾	3 000 ⁽⁵⁾	Banks et al. 1998
		D	520	30.4 ⁽²⁾	570 ⁽²⁾	Zelensky et al. 1993
	Switzerland	DW	360	< 2 ⁽⁵⁾	80.6	Deflorin et al. 2004, UNSCEAR 2000
	Switzerland	M	42	< 2 ⁽⁵⁾	< 10 ⁽⁵⁾	Deflorin et al. 2004
		D	345 ⁽¹⁾	145 ⁽²⁾	1 500 ⁽²⁾	Fernandez et al. 1992
		G	345 ⁽¹⁾	32 ⁽²⁾	43 ⁽²⁾	
	Germany	G + D	14	1.15	5.1	Gans et al. 1987
	China	G + D	110	1.4	13.4	Zhuo et al. 2001
	Brazil	G + D	88 ⁽¹⁾	0.08	667	Almeida et al. 2004
	France	G + D	54	8.7	24.4	Saumande et al. 1973
	Slovenia	G	500	0.51	4.2	Kobal et al. 1990
	Italy	DW	-	-	10.5	UNSCEAR 2000
	Colorado, north (USA)	D	566	18.6	<200	Zielinski et al. 1995
	Colorado, south (USA)	D	170	31.6	>200	Zielinski et al. 1995
	North America	DW	-	-	6.2	UNSCEAR 2000
²¹⁰ Pb (Bq/l)	Finland	D	1300	0.06	21	Salonen and Huikuri 2002,
		G	200	0.04	1.4	Mäkeläinen et al. 2002
	Germany	G + D	9	0.011	0.018	Gans et al. 1987
	United Kingdom	DW	-	-	0.2	UNSCEAR 2000
	Connecticut (USA)	G	5	-	0.05	Krishnaswami et al. 1982
²¹⁰ Po (Bq/l)	Finland	D	1300	0.07	16	Salonen and Huikuri 2002,
		G	200	0.01	1.3	Mäkeläinen et al. 2002
	Sweden	D	328	0.011 ⁽³⁾	0.95	Isam Salih et al. 2002
	Germany	G + D	10	0.008	0.06	Gans et al. 1987
	Florida (USA)	G	4	0.42	92	Upchurch 1987, Burnett et al. 1987

¹⁾ = number of drilled well and dug well samples all together.²⁾ = ²³⁸U concentration is calculated from total activity concentrations of uranium (²³⁸U and ²³⁴U) using isotope ratio of 2 and a factor 80.6 to convert Bq/l to µg/l.³⁾ = geometric mean⁴⁾ = median⁵⁾ = median and maximum values are estimated from cumulative frequency diagrams.

5. Accumulation of radionuclides in humans and recommendations for the maximum permissible activity concentration

The International Commission on Radiological Protection, ICRP, provides recommendations and guidance on all aspects of protection against ionising radiation, which are published in the Commission's own scientific journal, the *Annals of the ICRP*, also referred to in this study.

After entering the human body, radionuclides are typically accumulated in the skeleton, liver, kidney and soft tissues. Ingested radionuclides are not entirely retained in the human body. Therefore, the ICRP has presented fractional absorption, f_1 , which describes the proportion that is absorbed from drinking water and food by human body. The ICRP suggests that radionuclides in water are absorbed more easily than radionuclides incorporated in food (ICRP72 1996). The fractional absorption for different radionuclides is given for ^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po in Table 3.

Dose coefficients allow determination of the effective dose associated with radiation exposure in assessing the health risk to people. The dose coefficient is expressed in Sv/Bq, the effective dose equivalent per unit water activity concentration of the radionuclide. The annual effective dose is calculated taking into account the activity concentration of the nuclide (Bq/l), the dose coefficient (Sv/Bq) and the annual water consumption (l) according to equation 1.

$$\begin{array}{l} \text{Annual} \\ \text{effective} \\ \text{dose} \\ \text{(mSv/y)} \end{array} = \begin{array}{l} \text{activity} \\ \text{concentration} \\ \text{(Bq/l)} \end{array} \times \begin{array}{l} \text{dose} \\ \text{coefficient} \\ \text{(Sv/Bq)} \end{array} \times \begin{array}{l} \text{annual} \\ \text{water} \\ \text{consumption} \\ \text{(l/y)} \end{array} \times 1000 \quad (1)$$

The World Health Organisation (WHO) and Environmental Protection Agency (EPA) use the quantity of 2 litres per day water consumption for ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po for adults (World Health Organisation 2004, National Research Council 1999). ^{222}Rn is a noble gas and a part of it is removed during water usage (Nazaroff et al. 1987). The EPA has estimated that the amount of direct water usage is 0.6 litre per day, in which ^{222}Rn is not removed (National Research Council 1999). In Finland the value used for the total daily water consumption is 2.2 litres. The value of 0.5 litres is used for the direct use of tap water, from which ^{222}Rn is not removed (Guide ST 12.3 1993). The collective annual dose is calculated by multiplying the annual effective dose by the total number of users of a water source. The dose coefficients of ^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po are presented in Table 3.

Natural radioactivity in public water is restricted in Finland (Guide ST 12.3 1993, Decree 461/2000, Decree 401/2001). The safety requirement established in the Guide ST 12.3 is that the annual effective dose due to radioactive nuclides in household water shall not exceed 0.5 mSv. Some changes in the regulations will take place within a few years as a consequence of the EU drinking water directive issued by the European Union in 1998 and the implementation of its annexes in national regulations. The EU drinking water directive includes a reference dose of 0.1 mSv per year, including isotopes of uranium and radium. ^{222}Rn and its decay products, ^{210}Po and ^{210}Pb , are excluded from the reference dose. Recommendations for ^{222}Rn , ^{210}Po and ^{210}Pb are given in Commission Recommendation 2001. Values from the EU drinking water directive have been implemented in Finnish legislation as a decree. However, they will not take effect until separate instructions for monitoring methods and sampling frequencies have been set. The maximum permissible activity concentration for ^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po based on Guide ST 12.3, the EU Drinking Water Directive and Commission Recommendation are given in Table 3.

Except for ^{222}Rn , radioactive progenies produced in bone are assumed to follow the behaviour of the parent nuclide until removed from bone (ICRP67 1993). Outside the bone, nuclides behave according to their own biokinetics, which are described in chapters 5.1 – 5.5.

Table 3. The fractional absorptions, dose coefficient and maximum permissible activity concentration for ^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po (ICRP67 1993, ICRP72 1996, National Research Council 1999).

Radionuclide	Fractional absorption (f_1) for adults	Dose coefficient for adults, (Sv/Bq)	Maximum permissible activity concentrations for drinking water in Finland, Guide ST 12.3, (Bq/l)	Maximum permissible activity concentrations according to EU legislation, (Bq/l)
^{222}Rn	0.30	3.5×10^{-9}	300, 1000 ⁽¹⁾	100 – 1000 ⁽³⁾
^{226}Ra	0.20	2.8×10^{-7}	3	0.5 ⁽²⁾
^{238}U	0.02	4.5×10^{-8}	20	3.0 ⁽²⁾
^{234}U	0.02	4.9×10^{-8}	20	2.8 ⁽²⁾
^{210}Pb	0.20	6.9×10^{-7}	0.5	0.2 ⁽³⁾
^{210}Po	0.50	1.2×10^{-6}	3	0.1 ⁽³⁾

1) Recommendation for private well user, the decree 401/2001 issued by Finnish Ministry of Social Affairs and Health.

2) Council directive 98/83/EY (Drinking Water Directive).

3) EU Commission Recommendation 2001.

5.1 ^{222}Rn

A Finnish epidemiological study found no association between radon in drinking water and the risk of stomach cancer (Auvinen et al. 2005). The levels of radon exposure in that study was, however, relatively low and the sample size was small. There have been no other epidemiological studies in the world that could quantify the risk of ingested ^{222}Rn . Therefore, the cancer risk arising from ingested ^{222}Rn is derived from calculations of the dose absorbed by the tissues (National Research Council 1999).

Studies have established the level of ^{222}Rn absorption in the gastrointestinal tract and subsequent elimination via the lungs. In about an hour 95% of the initial ^{222}Rn exits through the lungs. Therefore, the main health risk from ^{222}Rn is caused directly to the stomach. The National Research Council (1999) has estimated that about 30% of the activity concentration of ^{222}Rn in the stomach was integrated in the walls of the stomach.

The short-lived progenies of ^{222}Rn (^{218}Po , ^{214}Pb , ^{214}Bi and ^{214}Po) together contribute 7.7% of the effective dose caused by ^{222}Rn , assuming that they are in radioactive equilibrium with ^{222}Rn in water (Council Directive 96/29/Euratom 1996, Kendall et al. 1988). The exception is when ^{222}Rn gas is aerated from water but ^{222}Rn daughters remain in the water. However, in this case the dose from short-lived ^{222}Rn progenies in aerated water is still less than 10% of the dose from the ^{222}Rn in the untreated water (Swedjemark et al. 1998).

According to Guide ST 12.3, the action limit for ^{222}Rn in public water is set to 300 Bq/l. In 2001 the Commission of the European Communities issued a recommendation on the protection of the public against exposure to ^{222}Rn in drinking water supplies (Commission Recommendation 2001). It set a reference level of 100 Bq/l for ^{222}Rn . A higher level may be adopted if national surveys show it necessary for implementing a practical ^{222}Rn reduction programme. If the activity concentration exceeds 1000 Bq/l, remedial action is justified on radiological protection grounds. This recommendation was taken into account in the decree 401/2001 issued by the Finnish Ministry of Social Affairs and Health. The action level 300 Bq/l of ^{222}Rn was given for units with less than 50 consumers. For private wells, the guideline was set to 1000 Bq/l.

5.2 ^{226}Ra

Finnish case-cohort studies have found no association between ^{226}Ra in drinking water and the increased risk of leukemia or stomach cancer (Auvinen et al. 2002, Auvinen et al. 2005). A separate study revealed that ingestion of radium was causally associated with leukemia in man (Lyman et al. 1985). However, the authors stated that further investigations are needed before a causal relationship

between ^{226}Ra in drinking water and human leukemia can be established. Other epidemiological studies have found an increased risk of osteosarcoma and radium in drinking water (Finkelstein 1994, Finkelstein and Kreiger 1996).

The ICRP has estimated that gastrointestinal absorption of radium from drinking water and food accounts for 15 – 21% of ingested radium. The same results were obtained from mock radium dial paint containing $^{224}\text{RaSO}_4$ (ICRP67 1993). Thus, the fractional absorption 0.2 was adopted for adults. The absorption of radium by children is greater than for adults during the rapid period of growth.

According to ICRP67 (1993), the behaviour of radium in the human body is similar to that of barium. Radium transfers from the gastrointestinal tract to the blood and lungs and generally follows the behaviour of calcium. However, the rate of movement between plasma, bone, soft tissues and urinary and faecal excretion differs from calcium. Significant amounts of radium pass through the intestines and are excreted in the faeces. In the body, radium is mainly deposited and retained in bone and soft tissues. Initially, skeletal retention decreases by about 10% during one month, but later it decreases gradually by 0.5 – 1% over 25 years. After ingestion the soft tissues may represent 20% or more of the total activity concentration of radium, but later the amount of radium in soft tissues decreases. (ICRP67 1993)

The EU drinking water directive lays down for waterworks a reference dose of 0.1 mSv per year, from which ^3H , ^{40}K , ^{222}Rn and ^{222}Rn progenies are excluded (Council directive 98/83/EY 1998). Thus, in practice this includes isotopes of uranium and radium, since thorium is poorly soluble in Finnish groundwater (Tarvainen et al. 2001). Using the dose coefficient factors presented in Table 3 and a daily water consumption of two litres, a reference dose of 0.1 mSv per year corresponds to an activity concentration of ^{226}Ra of 0.5 Bq/l.

5.3 ^{234}U , ^{235}U and ^{238}U

There are insufficient data in the world regarding the carcinogenicity of uranium in humans and experimental animals (World Health Organization 2004). Finnish epidemiological studies have not found associations between uranium in drinking water and the increased risk of leukemia or stomach cancer (Auvinen et al. 2002, Auvinen et al. 2005).

For uranium, a fractional absorption of 0.02 has been adopted for adults (ICRP69 1995). The fractional absorption of uranium from drinking water has varied in the range of 0.005 – 0.06 and in dietary balance in the range of 0.004 – 0.04.

According to ICRP69 (1995), uranium entering the blood is first taken up by soft tissues or excreted in urine. The majority of uranium is excreted during a few months, but a few percent is retained for a period of years. From soft tissues, uranium is transferred to the kidneys and skeleton. In the skeleton the behaviour of uranium (UO_2^{2+}) is similar to that of alkaline earths. Uranium exchanges with Ca^{2+} on the surface of bone mineral and it accumulates in the highly concentrated area of growth. Uranium may also diffuse into the bone volume. The liver accumulates 1.5 – 2% of uranium and most of it is removed over a few weeks. Soft tissues other than the liver and kidneys contain about 5% of uranium and after over a year only 0.3% of it remains.

In addition to radioactivity, uranium has chemical toxicity that predominately affects the kidneys (Auvinen et al. 2002, Kurttio et al. 2002, Kurttio et al. 2005). According to present knowledge, the uranium concentration is limited mainly by chemical toxicity rather than the effective dose (World Health Organization 2004). In 2003 the WHO proposed a provisional guideline of 15 $\mu\text{g/l}$ (0.19 Bq/l) for ^{238}U , which was based on its chemical toxicity.

The EU drinking water directive lays down for waterworks a reference dose of 0.1 mSv per year (Council directive 98/83/EY 1998). Using the dose coefficient factors presented in Table 3 and a daily water consumption of two litres, it correspond to an activity concentration of ^{234}U and ^{238}U of 2.8 and 3.0 Bq/l, respectively. The EU drinking water directive does not give an exact guideline for ^{238}U concentration. Using the $^{234}\text{U}/^{238}\text{U}$ ratio of 1.5, it corresponds to a ^{238}U mass concentration of 100 $\mu\text{g/l}$.

5.4 ^{210}Pb

There have been no epidemiological studies in the world that could quantify the risk of ingested ^{210}Pb . ^{210}Pb is absorbed more easily from drinking water than from food (ICRP67 1993). Typical values for the fractional absorption of ^{210}Pb in adults have been in the range of 0.03 – 0.14. In ICRP publication 67 (1993), a value of 0.20 was adopted for adults.

ICRP67 (1993) estimated that after ^{210}Pb enters the human body, 55% is found in the blood, 15% in the liver and 10 – 15% in the skeleton. More than 99% of ^{210}Pb in blood is associated with red cells, where the activity decreases dramatically over 15 – 20 days. The biological half-life in the liver is only few weeks, where ^{210}Pb is transferred to the urine, faeces and skeleton. The ^{210}Pb content of the skeleton increases throughout life. The behaviour of ^{210}Pb in the skeleton is similar to that of heavier alkaline earth elements. The exception is the deposition of ^{210}Pb in the skeleton, which is slower than for the other heavier alkaline earth elements due to competition with other tissues and fluids. ^{210}Pb

decays via ^{210}Bi to ^{210}Po . These are assumed to follow the behaviour of the parent nuclide until they are removed from bone. ^{210}Po is retained in the liver, kidneys, red bone marrow and other tissues. ^{210}Bi is rapidly excreted in urine.

In 2001 the Commission of the European Communities gave a recommendation on the protection of the public against exposure to ^{222}Rn in drinking water supplies (Commission Recommendation 2001). The recommendation has given a reference activity concentration of 0.2 Bq/l for ^{210}Pb .

5.5 ^{210}Po

There have been no epidemiological studies in the world that could quantify the risk of ingested ^{210}Po . Considerably less data are available on the fractional absorption of ^{210}Po compared to that of ^{210}Pb (ICRP67 1993). The value of 0.50 has been adopted for adults. Typical reported values for the fractional absorption of ^{210}Po have been 0.3 – 0.8 for adults consuming reindeer or crabmeat. The dose coefficient for ^{210}Po is the second highest from all radionuclides after ^{227}Ac (Council Directive 96/29/Euratom 1996). Thus, it is important to examine the levels of ^{210}Po in the environment.

ICRP67 (1993) estimated that over 50% of ^{210}Po entering the blood is excreted in faeces. The rest is transferred to the liver, kidneys, spleen and all other tissues in fractions of 0.1, 0.1, 0.1 and 0.7, respectively. The whole-body retention of ^{210}Po has been estimated to be 30 – 50 days (ICRP67 1993).

In 2001 the Commission of the European Communities gave a recommendation on the protection of the public against exposure to ^{222}Rn in drinking water supplies (Commission Recommendation 2001). The recommendation has given a reference activity concentration of 0.1 Bq/l for ^{210}Po .

6. Radionuclide removal methods from drinking water

Significant effective doses can be received from drinking water due to natural radioactivity. So far, the highest effective annual dose from drinking water has been 70 mSv (Mäkeläinen et al. 2002, Salonen and Huikuri 2002). However, the dose can be restricted. Possible options are to use a water source with a low activity concentration of radionuclides, such as water from waterworks, or to treat the water with treatment equipment.

The removal of natural radionuclides from Finnish groundwater by various methods was examined in three separate studies during the years 1995 and 2001 (Annamäki and Turtiainen 2000, Myllymäki et al. 1999, Vesterbacka et al. 2003). A summary of the main results obtained in these studies is presented in Table 4. The removal of natural radionuclides by ion exchange has also been studied in the doctoral thesis of Vaaramaa (Vaaramaa 2003). That work concentrated on organic and inorganic ion exchange materials and experiments in the laboratory. The interest in this study was put on commercial available ion exchange resin and studies in the field.

6.1 ^{222}Rn removal by aeration and activated carbon filtration

^{222}Rn can be efficiently removed by applying aeration or granular activated carbon filtration. Both of these methods remove over 90% of ^{222}Rn from water (Turtiainen et al. 2000a, Vesterbacka et al. 2003). In aeration, water can be released into air or air can be released into the water. A common method to remove ^{222}Rn is to spray untreated water into the storage tank with a fine mist spray nozzle. In granular activated carbon filtration the dissolved ^{222}Rn atoms are retained on activated carbon during filtration. ^{222}Rn decays in the unit and forms decay products inside the granular activated carbon unit. These decay products are also retained in the unit and emit gamma rays, which makes the unit a source of radiation. The dose rate obtains its maximum value after three weeks of usage. The dose rate near the filter is dependent on the activity concentration of ^{222}Rn in raw water and on water consumption. Due to this disadvantage, granular activated carbon filtration is recommended in Finland only for an activity concentration of ^{222}Rn less than 5000 Bq/l. In addition, units are recommended to be installed in the utility room in a separate building or in connection with the well. Aeration is a suitable method for all activity concentrations of ^{222}Rn .

6.2 ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po removal

Long-lived radionuclides (^{234}U , ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po) cause a dose only by ingestion. Therefore, they only need to be removed from water used for drinking and cooking.

The treatment methods used for ^{234}U and ^{238}U removal are conventional coagulation and filtration, lime-softening, ion exchange, activated aluminium oxide filtration, activated carbon filtration and reverse osmosis (Fox and Sorg 1987, Sorg 1990, Turtiainen et al. 2000b, Vesterbacka et al. 2003, White and Bondietti 1983). The most efficient and frequently used method in private homes for ^{234}U and ^{238}U removal has been ion exchange. The removal efficiency attained by using strong base anion (SBA) resin has been over 90% (Fox and Sorg 1987, Zhang and Clifford 1994). The ion exchange method is discussed in more detail in chapter 6.2.1.

The available technologies for ^{226}Ra removal include ion exchange, lime-softening and reverse osmosis. Hydrous manganese oxide filtration is also capable of removing 65% – 90% of ^{226}Ra (Qureshi and Nelson 2003, Zapecza and Szabo 1986). However, the most efficient removal methods have been ion exchange using strong acid cation (SAC) resin and reverse osmosis. The removal efficiencies attained by ion exchange and reverse osmosis have been 99% (Huikuri et al. 1998, Snoeyink et al. 1987, Snyder et al. 1986). ^{226}Ra was also partly removed from water by an anion exchange resin (Table 4), probably because the resin removes organic matter from groundwater to which ^{226}Ra is bound.

The removal of ^{210}Pb and ^{210}Po is more demanding, since these radionuclides occur in groundwater bound to various sizes of particles (Lehto et al. 1999, Vaaramaa et al. 2003). Reliable and efficient removal of ^{210}Po and ^{210}Pb is not achievable using ion exchange or activated carbon units, because they do not completely retain the particles in groundwater to which the radionuclides are bound. The size distribution of particle-bound ^{210}Po and ^{210}Pb varies depending on the chemical composition of the water. The efficient removal of ^{210}Po and ^{210}Pb is reverse osmosis. Removal efficiencies for stable lead and ^{210}Po have ranged from 96 to 98% (Fox and Sorg 1987, USEPA 1991). Reverse osmosis is a membrane filtration technique, which uses pressure to force water molecules through a semi-permeable membrane. Systems using this method are effective in removing constituents that have a molecular weight of greater than 100 Daltons (0.1–1 nm). The separation of ions with reverse osmosis is aided by charged particles, the size and shape of the molecules, the hydrophilic nature of the molecule and the separating capacity of the membrane.

Table 4. Different methods for removing ^{222}Rn , ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po from drinking water and reported removal efficiencies (%) (Annanmäki and Turtiainen 2000, Myllymäki et al. 1999, Vesterbacka et al. 2003). Of the presented methods, ion exchange, activated aluminium oxide filtration and reverse osmosis were tested by the author.

Treatment method	Removal efficiency (%)					Side effects
	^{222}Rn	$^{234,238}\text{U}$	^{226}Ra	^{210}Pb	^{210}Po	
Aeration	60 – 99	-	-	-	-	Removes CO_2 , pH may increase, Fe and Mn precipitate, O_2 enrichment.
Granular activated carbon filtration	> 99	0-100 ¹	0-95 ²	30-100 ²	50-100 ²	Reduced Fe, turbidity, organic matter, deterioration of hygienic quality possible.
Activated aluminium oxide filtration	-	80-100	>90	>80	>80	Removes F and some amounts of Fe and Mn, Al concentration in the treated water may increase
Ion exchange - SBA resin ³ - SBA and SAC resin ³	-	>95	35-60	20-70 ²	50-70 ²	Reduced NO_3 , SO_4 , organic matter, Fe, Mn, hardness, increases water salinity deterioration of hygienic quality possible.
	-	>95	95-98	20-90 ²	50-70 ²	Reduced Fe, Mn, hardness, increased water salinity, Deterioration of hygienic quality possible.
Reverse osmosis	-	>99	>99	>95	>95	Reduces total dissolved solids up to 98%, treated water corrosive.

¹⁾ high adsorption can be achieved only a few months after installation. After couple of month's adsorption is close to 0%.

²⁾ depends on chemical composition of the groundwater

³⁾ SBA = strong base anion, SAC = strong acid cation

6.2.1 Ion exchange

Ion exchangers have been used to remove uranium from mine water for many years (Sorg 1990). It is a simple and cost effective method. Moreover, it has a high capacity to remove uranium from water over the other elements occurring in groundwater (Zhang and Clifford 1994). Ion exchangers have also been applied to uranium removal from drinking water (Vesterbacka et al. 2003, Zhang and Clifford 1994).

The most common ion exchange resin used for uranium removal is strong-base anion resin. The matrix composition of the resin is styrene–divinylbenzene (DVB) copolymer. The important resin property is the proportion of DVB to styrene used in the initial monomer mix, which affects the capacity, ion selectivity, rate of exchange and stability of the resin. Resins with very low crosslinking have the maximum theoretical concentration of active groups. The degree of crosslinking in commercial resins is typically between 2–20%. The active group in strong-base anion resins is the quaternary ammonium group $-\text{N}(\text{CH}_3)_3^+$ (Cohen 1989).

The physical structure of the resin can be either macroporous or gel-type. Styrene–DVB copolymers are produced by suspension-polymerization of the monomers in aqueous media. These products are referred as gel-type resins. In order to avoid a gel-type structure, each bead can be precipitated during polymerization. The result is a two-phase structure that is less sensitive to swelling.

6.2.2 Principle of ion exchange

When an ion exchange resin comes into contact with water, the components in the water change place with those in the resin. In uranium removal, uranium-rich water passes through the bed of a strong base anion exchange resin in the chloride form. The ion exchange reactions between uranium complexes and resin are the following:



R represents an anion exchange site, a quaternary ammonium group, on the resin. An equilibrium reaction takes place, meaning that uranium complexes are retained on the resin and an equivalent amount of chlorine ions are released into the water. Several factors affect the ion exchange process, the main factors being the concentration of ions in the groundwater, the mass velocity of water flow, size of the resin particles, diffusion coefficients, crosslinking and temperature (Cohen 1989).

7. Methods for the determination of natural radionuclides in water

7.1 ^{222}Rn

The most frequently used determination method for ^{222}Rn is measurement by liquid scintillation spectrometry (Haaslahti et al. 2000, Salonen 1993a, Salonen and Hukkanen 1997, Spaulding and Noakes 1994). ^{222}Rn can be measured either from two-phase cocktails, where ^{222}Rn is extracted from water into immiscible cocktails, or in a homogeneous gel where water is mixed with a liquid scintillation cocktail. Other ^{222}Rn measurement techniques reported in literature are a delay-coincidence liquid scintillation counting system, an activated charcoal ^{222}Rn collector, a degassing Lucas Cell and an ionization chamber system (EPA 1999). In large volume samples, ^{222}Rn can also be detected by gamma spectrometry of its daughter products.

7.2 Gross alpha and beta

Gross alpha and beta measurements are widely used in the screening of alpha and beta activity in drinking water (Burnett et al. 1998, Burnett et al. 2000, ISO9696 1992, ISO9697 1992, Parsa et al. 2000, Salonen 1993b, Salonen 1994, Sanchez-Cabeza and Pujol 1995, Wong et al. 1999). They are often inexpensive and simple methods. They can also be a waste-free approach for screening total radioactivity when liquid scintillation cocktails are not used. The main principle in gross alpha and beta determination is to acidify the water sample and evaporate it almost to dryness. After evaporation the sample is dissolved in a small volume of acid and is either transferred to a liquid scintillation vial for measurement by a liquid scintillation counter or is directly transferred to the counting planchette of an alpha and beta proportional counter.

Various types of equipment are used for *gross alpha* measurement: liquid scintillation counters, silver activated zinc sulfide scintillation screens and silicon surface barrier detectors or proportional counters (windowless). For *gross beta* measurement the equipment used include liquid scintillation counters, Geiger counters or gas flow proportional counters (Cook et al. 2003).

Several important factors should be considered in gross alpha and beta analysis:

1. The term gross does not necessarily mean total. Often, gross alpha and beta measurements exclude ^{222}Rn and its short-lived progeny from the analysis.

2. Sample thickness affects the detector efficiency and quantitative evaluation of mass adsorption influences the measurement accuracy. This is a problem when using a silver-activated zinc sulfide scintillation screen, silicon surface barrier detector, Geiger counter or proportional counter.
3. A liquid scintillation counter equipped with a pulse shape analyzer and spectrometer may also give more information than just the activity concentrations of gross alpha and beta. More detailed information on nuclide-specific composition can be evaluated from the alpha and beta spectrum and in some cases quite accurate activity concentrations of ^{238}U and ^{226}Ra can be determined.
4. The gross beta is difficult to calibrate accurately, since the counting efficiency depends on the energy of the measured radionuclide. Therefore, for accurate calibrations the composition of beta-active elements in drinking water should be known beforehand.
5. Artificial radionuclides need to be taken into account in measurements of surface water.

7.3 ^{226}Ra

The most conventional method for ^{226}Ra determination is BaSO_4 co-precipitation or its modifications, which are still in use in some laboratories across the world (Lozano et al. 1997, Parsa and Hoffman 1992). ^{226}Ra can be determined from water by liquid scintillation counting of the ^{222}Rn daughter product ^{214}Po (Salonen 1993b, Salonen and Hukkanen 1997). This typically includes volume reduction and aeration, after which the sample is sealed and stored for approximately 3 to 4 weeks to allow ^{222}Rn ingrowth. Other techniques for ^{226}Ra separation include ^{226}Ra selective membranes, extraction into scintillation cocktail, cation exchange chromatography, Diphonix ion exchange resin and electrodeposition (Balnco Rodriguez et al. 2000, Burnett et al. 1995, Clifford and Higgins 1992, Crespo and Jimenez 1997, Durecová 1997, Durecová et al. 1999, Nour et al. 2004, Purkl and Eisenhauer 2003, Saito et al. 2003, Smith et al. 1997). Manganese dioxide (MnO_2) is also used to concentrate ^{226}Ra from water (Baeza et al. 1998, Eikenberg et al. 2001, Moon et al. 2003). The final sample is measured using a liquid scintillation counter, an alpha spectrometer, a proportional counter, a silver activated zinc sulphide scintillator $\text{ZnS}(\text{Ag})$, a HR-ICP mass spectrometer or a gamma spectrometer, depending on the chemical form of the final sample.

7.4 ^{234}U , ^{235}U and ^{238}U

Uranium can be separated from other interfering radionuclides by using, for example, an extractive scintillation technique, ion exchange, electrodeposition or extraction chromatography (Blackburn and Al-Masri 1994, Gascoyne 1981, Gupta et al. 2002, Liberman and Moghissi 1968, Sill 1981, Sill 1987, Weber et al. 1999, Yonghui et al. 1998, Zaki 2002). Good measurement techniques for low-level ^{238}U determination are ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and semi-conductor alpha spectrometry. Liquid scintillation spectrometry and PERALS (Photon Electron Rejecting Alpha liquid Scintillation) spectrometry have also been utilized for ^{234}U and ^{238}U measurement (Duffey et al. 1997, Leyba et al. 1994, McKlveen and McDowell 1984, Venso et al. 1993).

ICP-MS is the most recent technique for determining uranium isotopes from environmental samples (Baglan et al. 1999, Manninen 1995, Sahoo et al. 2002). Sample preparation in that technique is very simple for water samples, since time consuming analytical work is not needed. In alpha spectrometry, uranium isotopes always need to be chemically separated from other interfering radionuclides and the sample preparation must be almost without mass. In measurement using liquid scintillation spectrometry, uranium must also be separated from other interfering radionuclides in order to attain sufficient peak resolution and thus obtain an accurate activity concentration.

7.5 ^{210}Pb

There are many useful separation methods for the determination of ^{210}Pb in environmental samples (Al-Masri et al. 1997, Figgins 1961, Garcia-Orellana and Garcia-León 2002, Häsänen 1977, Katzlberger et al. 2001, Murray et al. 1987, Qingjiang et al. 2001, Tokieda et al. 1994, Vajda et al. 1997). The activity concentration of ^{210}Pb can be measured directly by gamma spectrometry from the 46.5-keV photo peak (Murray et al. 1987). However, measurement is not always simple due to self attenuation in the sample at a low energy and low gamma ray intensity. The limit of detection is often too high for low-level activity measurements without pretreatment. Typically, preconcentration is needed as well as the chemical separation of ^{210}Pb from other naturally occurring radionuclides. After separation, the activity concentration of ^{210}Pb can be measured using liquid scintillation spectrometry, proportional counting, and alpha spectrometry via ^{210}Po or gamma spectrometry. A classical method is based on the deposition of its daughter nuclide, ^{210}Po , on a silver or nickel disk and measurement with alpha spectrometry or a proportional counter (Figgins 1961, Häsänen 1977). With alpha spectrometry it is possible to achieve a very low limit of detection, down to 0.1 mBq per sample. The most recent methods have been based on extraction

chromatography (Eichrom's Pb resin), liquid-liquid extraction of ^{210}Po followed by ^{210}Pb determination together with or via ^{210}Bi after a sufficient ingrowth time (Katzlberger et al. 2001, Vadja et al. 1997). The limit of detection is higher than with alpha spectrometric measurement, but the analysis time is much shorter due to the faster ingrowth of ^{210}Bi compared to ^{210}Po .

7.6 ^{210}Po

A classical method for ^{210}Po determination is spontaneous deposition on a silver or nickel disk (Feldman and Frisch 1956, Figgins 1961, Flynn 1968, Garcia-Orellana and Garcia-León 2002, Häsänen 1977, Johns et al. 1979, Karali et al. 1996, Tokieda et al. 1994). The sample is measured by alpha spectrometry using a semiconductor or ZnS(Ag) α -particle detector. Other separation methods for ^{210}Po are extraction chromatography, electrodeposition techniques, extraction into scintillation cocktail, metal-containing membranes and anion-exchange methods (Karali et al. 1996, Katzlberger et al. 2001, Miura et al. 2000, Moskvina et al. 1993, Pacer 1983, Qingjiang et al. 2001, Suganuma 1995, Vadja et al. 1997, Wallner 1997).

8. Sample collection and analytical methods used in this study

8.1 Sample collection

Groundwater samples analysed in this work were fresh groundwater samples collected from either drilled wells or dug wells. Samples were collected by a STUK employee and by the local health authorities or the well owner according to the instructions given by STUK. Sampling methods varied depending on the objectives of the study.

Before collecting a ^{222}Rn sample, water was allowed to run for 15 – 30 minutes in order to ensure that the water came directly from the well and was not delayed in the pipe system or pressure tank. ^{222}Rn samples were taken into glass vials, which were prefilled with a liquid scintillation cocktail, Packard Ultima Gold XR (Publication I).

^{222}Rn subsamples were taken from plastic bottles containing well-water samples with the intention of studying ^{222}Rn leakage from the bottles during sample transport. The activity concentration of ^{222}Rn was used for calculating ingrowth of the activity concentration of ^{210}Pb during sample transport. The first subsample was taken before closing the cap of the plastic bottle in the field and the second subsample in the laboratory immediately after opening the cap (Publications I and III).

Samples for the determination of long-lived radionuclides (^{234}U , ^{238}U , ^{226}Ra , ^{210}Po and ^{210}Pb) were collected into polyethylene plastic bottles from the tap. In the laboratory, the water samples were acidified in 0.05M HCl (4.5 ml for one-litre sample) and aerated for one hour to remove ^{222}Rn from the water sample (Publications I, IV and V). In the study in which particle-bound ^{210}Pb and ^{210}Po were examined, water samples were not acidified before filtering in order not to destroy the particles in groundwater (Publication II).

When the temporal variation in the activity concentration of ^{210}Pb during the day was investigated, samples were collected four times a day from the same test site: in the morning, the afternoon and the early and late evening. In the late evening, a parallel sample was collected using the standard sampling method, where water was allowed to run for 15 – 30 minutes before collecting the sample in order to ensure that the water came directly from the well and was not delayed in the pipe system or pressure tank (Publication III).

In the study of the occurrence of ^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po in groundwater, the water samples were collected from randomly selected wells (Publication I). The criterion for selecting the well was that the household used

water from the private well as a permanent source of drinking water. In the studies where the removal of ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po and sampling of ^{210}Pb and ^{222}Rn was examined, the criteria for selecting the wells was high radioactivity in the groundwater and the use of removal equipment in the private home for removing radioactivity from the drinking water (Publications II, III and V). More detailed descriptions of the sample collection methods are presented in each publication.

8.2 Analytical methods

Determination methods used in this study for analysing ^{222}Rn , ^{238}U , ^{234}U , ^{210}Pb and ^{210}Po have been accredited according to ISO standard 17025 (European Standard EN ISO/IEC 17025:2000). ^{226}Ra , gross alpha and ^{210}Pb determination using extraction chromatography and liquid scintillation spectrometry are not accredited, but the quality of these methods is controlled by the same methods used in the accredited determinations. Lower limits of detection for each method are calculated using either the Currie definition or the equation presented by the EPA (Currie 1968, Johns et al. 1979). At the present time, ISO standard 11929-7 is available and the detection limit for ionizing radiation measurement should be calculated according to this (ISO 11929-7:2005). Short descriptions of the determination methods are presented in the following.

8.2.1 ^{222}Rn

The activity concentration of ^{222}Rn was determined with a liquid scintillation spectrometer (1414 Guardian, Wallac). Ten millilitres of groundwater were added to a glass vial which was equipped with a cap containing aluminium foil and pre-filled with 12 ml of Ultima Gold™ XR (Packard) liquid scintillation cocktail (Salonen 1993a, Salonen and Hukkanen 1997). The activity concentration of ^{222}Rn was calculated from the alpha spectrum using a counting efficiency of $290 \pm 5\%$ (consisting of ^{222}Rn , ^{218}Po and ^{214}Po). The lower limit of detection at the 95% confidence level with the spectrometer was 0.17 Bq/l for 0.01 litres of water and a 60-minute counting time.

8.2.2 Gross alpha

The gross alpha activity concentration of was determined from all samples (Salonen 1993b, Salonen and Hukkanen 1997). The sample for gross alpha activity determination was prepared by evaporating 38 ml of water to dryness with a freeze-dryer in a teflon-coated polyethylene vial (Zinsser®). The residue

was dissolved in 1 ml of 0.5M HCl and then 21 ml of scintillation cocktail (Optiphase HiSafe 2, Wallac) was added. The sample was counted with a counting time of six hours one month after sample preparation. During that time ^{226}Ra attains equilibrium with ^{222}Rn and its short-lived daughters.

Gross alpha activity was determined with a low-background liquid scintillation spectrometer (1220 QuantulusTM) equipped with an anticoincidence guard counter and a pulse shape analyser (PSA). The gross alpha activity concentration was calculated from the alpha spectrum by using a wide alpha window (window W_B) that covers nearly all the alpha peaks (Figure 6). The alpha counts due to ^{222}Rn and its short-lived daughters were subtracted from the total counts measured in the wide alpha window on the basis of the counts measured in the narrow window (window W_A), which was set on the area of the separate peak caused by ^{214}Po (due to its high alpha energy of 7.7 MeV). The subtraction of their counts was possible because ^{214}Po was in equilibrium with ^{222}Rn and its other short-lived daughters. The lower limit of detection for gross alpha activity was 0.02 Bq/l at the 95% confidence level. The equation used for the calculation of gross alpha activity is presented below.

$$A_{\text{Gross-}\alpha} (\text{Bq/l}) = \frac{(W_B - bg) - 3.2 \times (W_A - bg)}{60 \times V \times \text{eff}} \quad (4)$$

where W_B is the count (cpm) from the wide alpha window (typically channels 580 – 800), W_A is the count (cpm) from the narrow alpha window (typically channels 735 – 800), V is the sample volume (l), eff is the counting efficiency (98%) and bg is the background count (cpm). The term 3.2 is the constant obtained from calibration.

8.2.3 ^{226}Ra

^{226}Ra was determined by liquid scintillation spectrometry via ^{222}Rn and its short-lived daughters from the gross alpha spectrum (Salonen 1993b, Salonen and Hukkanen 1997). The activity concentration of ^{226}Ra was calculated on the basis of the counts measured in a window set on the area of the ^{214}Po peak (Figure 6). This gives accurate results for ^{226}Ra , since no other natural or artificial radionuclides have alpha emissions in the same energy range. It was therefore not necessary to radiochemically separate ^{226}Ra from other nuclides and carefully purify it. The counting efficiency of ^{214}Po (and thus of ^{226}Ra) in the selected window was $86 \pm 2\%$. The lower limit of detection for ^{226}Ra was 0.01 Bq/l for a six-hour count

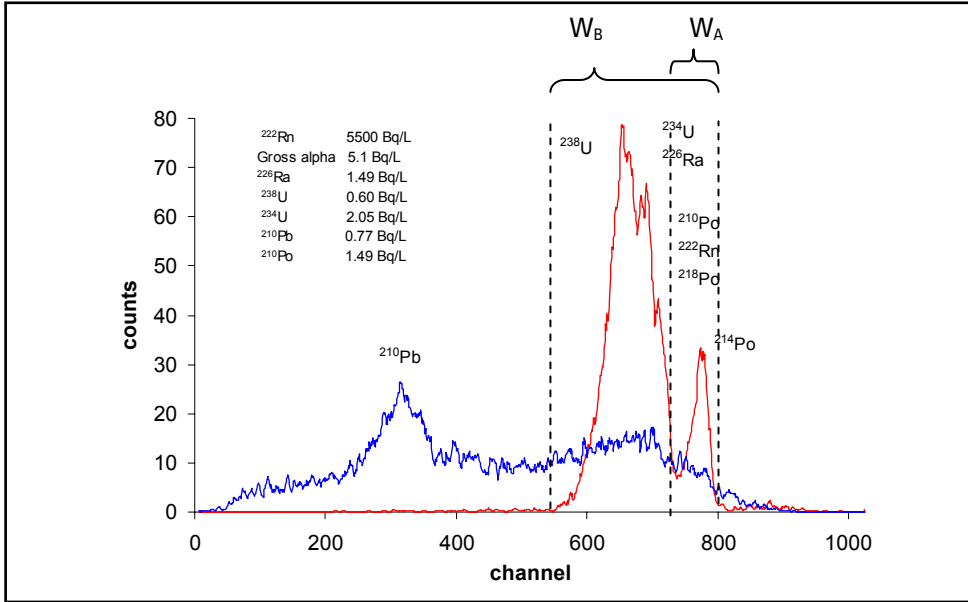


Figure 6. The alpha and beta spectra of drilled well water samples measured with a Quantulus™ 1220 spectrometer (Wallac).

at the 95% confidence level. The equation used for calculation of the activity concentration of ^{226}Ra is presented below.

$$A_{^{226}\text{Ra}} (\text{Bq/l}) = \frac{(W_A - bg)}{60 \times V \times \text{eff}} \quad (5)$$

where W_A is the count (cpm) from the narrow alpha window, V is the sample volume (l), eff is the counting efficiency of ^{214}Po (86%) and bg is the background count (cpm).

8.2.4 ^{234}U and ^{238}U

^{234}U and ^{238}U were determined using three methods: calculation from gross alpha determination, by radiochemical separation followed by alpha spectrometry and using ICP-MS technique. Measurements using ICP-MS were performed at the Geological Survey of Finland (GTK). The three methods gave reliable results that were comparable with each other, which has been confirmed by comparison measurements (Gustavsson et al. 2001).

^{234}U and ^{238}U from gross alpha

The combined activity concentrations of ^{234}U and ^{238}U were first calculated from the gross alpha activity. A good estimate of the ^{238}U concentration was obtained if the gross alpha activity was mainly caused by ^{234}U and ^{238}U isotopes, ^{226}Ra and ^{210}Po . The uranium content (sum of ^{238}U , ^{235}U and ^{234}U activity concentrations) was calculated by subtracting the counts due to ^{226}Ra from the gross alpha counts (chapter 8.2.2). The activity concentration of ^{210}Po is not known but its concentration is rarely high in Finnish groundwater. The lowest concentration of ^{238}U that could be estimated in most cases with good accuracy was 10 $\mu\text{g/l}$, corresponding to a gross alpha activity of 0.025 Bq/l.

Radiochemical separation of ^{234}U and ^{238}U

The activity concentration of ^{234}U and ^{238}U was determined by using radiochemical separation and alpha spectrometry. The water sample was first enriched by Fe hydroxide co-precipitation. The iron hydroxide precipitate was separated from the solution and dissolved in concentrated HCl. ^{234}U and ^{238}U were then separated from the other radionuclides by ion exchange (using Dowex 1x8, 50/100 mesh). Before anion exchange the resin was conditioned with 40 ml of concentrated HCl. ^{234}U and ^{238}U were eluted from the column using 40 ml of dilute 0.1M HCl acid, which was evaporated to dryness. The residue was dissolved in 5ml of 1M HCl to which 0.5ml of $\text{CeCl}_3 \times 7 \text{ H}_2\text{O}$ was added. This corresponded to a cerium amount of 50 μg . After cerium addition, ^{234}U and ^{238}U were reduced to the +IV oxidation state by TiCl_4 . The counting planchet was prepared by co-precipitating ^{234}U and ^{238}U on a 0.1 μm Metrical polypropylene membrane as CeF_3 using 1.5 ml concentrated HF (Liberman and Moghissi 1968, Sill 1981, Sill 1987). The diameter of membrane was 25 mm and the effective precipitation area 283.5 mm^2 . The sample was then counted by alpha spectrometry (AlphaAnalyst, Genie2000). The minimum detectable activity (MDA) was 0.5mBq/l for one litre of water and a 1000-minute counting time. ^{232}U was used as a chemical yield tracer. The recovery of ^{232}U was typically 70 – 100%.

 ^{238}U by ICP-MS technique

The ^{238}U concentration was determined by ICP mass spectrometry in the analytical laboratory of the Geological Survey of Finland. Samples (100 ml) were acidified using 0.5 ml of concentrated HNO_3 acid. The minimum detectable concentration was 0.01 $\mu\text{g/l}$, corresponding to 124 $\mu\text{Bq/l}$ (Tarvainen et al. 2001).

8.2.5 ^{210}Po

The determination of ^{210}Po was based on the spontaneous deposition of ^{210}Po activity on a silver disc (Feldman and Frisch 1956, Flynn 1968, Häsänen 1977). The activity of ^{210}Po was determined by alpha spectrometric measurement. ^{209}Po was used as tracer and it was added one day before ^{210}Po deposition. The minimum detectable activity (MDA) was 0.01 Bq/l for a 0.5 litre water sample and a 1000-minute counting time. The recovery of ^{209}Po was typically 70 – 100%.

8.2.4 ^{210}Pb

Two different methods were used in this study for analysing the ^{210}Pb activity concentration in drinking water. One was based on the spontaneous deposition of ^{210}Po activity on a silver disc and alpha spectrometry and the other was based on extraction chromatography and liquid scintillation spectrometry (Häsänen 1977, Vadja et al. 1997). Both methods have advantages over each other. The lower limit of detection attained using spontaneous ^{210}Po deposition on a silver disk is much lower than that in extraction chromatography. However, the disadvantage is its very long analysis time. In extraction chromatography the results are available in a month, where as in spontaneous ^{210}Po deposition on a silver disk at least six months is needed for sufficient in-growth of ^{210}Po from ^{210}Pb .

Determination of ^{210}Pb via spontaneous deposition on a silver disk

Two ^{210}Po depositions are needed to determine the activity concentration of ^{210}Pb . The solution remaining from the first ^{210}Po deposition was stored for at least six months to allow the in-growth of ^{210}Po from ^{210}Pb . During that time, 59% of the radioactive equilibrium was reached. The second ^{210}Po deposition was then carried out from the same solution as the first ^{210}Po deposition. ^{208}Po was used as tracer and was added in most cases one day before the second ^{210}Po deposition. The ^{210}Pb activity concentration in the water was calculated using results from the second ^{210}Po depositions according to equation 6.

$$A_{Pb} = \frac{A_{Po2}}{(e^{-\lambda_{Pb} \times \Delta t} - e^{-\lambda_{Po} \times \Delta t})} \times e^{-\lambda_{Pb} \times \Delta t} \quad (6)$$

where A_{Po2} is the activity concentration of ^{210}Po after in-growth time Δt and λ_{pb} and λ_{po} are the decay constants of ^{210}Pb and ^{210}Po , respectively. The method is also discussed in more detail in Publication IV.

Determination of ^{210}Pb using extraction chromatography and liquid scintillation counting

^{210}Pb was separated from other radionuclides using extraction chromatography (Vadja et al. 1997). The samples were counted using a Quantulus 1220 liquid scintillation spectrometer with a high counting efficiency and a low beta background. The water sample was first enriched by Fe hydroxide co-precipitation. The iron hydroxide precipitate was separated from the liquid and dissolved in dilute nitric acid. ^{210}Pb was separated from the other radionuclides by extraction chromatography (Eichrom's Sr resin). The sample was counted after a 30-day period during which ^{210}Bi attained radioactive equilibrium with ^{210}Pb . The result was then calculated from ^{210}Bi and ^{210}Pb together, which were observed with a counting efficiency of 190%. The minimum detectable activity was 0.05 Bq/l at the 95% confidence level for a 0.5-litre water sample and a 180-minute counting time. The inactive lead was used in the yield determination and its concentration was determined with an atomic absorption spectrophotometer (AAS). In publication III, a false value for the minimum detectable activity has been given.

8.3 Filtering experiments

The distribution of ^{210}Po and ^{210}Pb in various particle-size fractions was studied by filtering water through membranes with pore sizes ranging from 450 nm to 100 kDa. The unit of weight is the Dalton (Da), one-twelfth the weight of an atom of ^{12}C . The weight of 100 kDa corresponds to some tens of nm (at maximum 100 nm) in the pore opening scale. The use of filters and membranes to study particle-bound radionuclides is only semi-qualitative, since this method includes several uncertainties in the evaluation of results (Stumm and Morgan 1996). Generally, the way the filtering experiment is performed is important. Firstly, although most particles larger than the pore size are retained on the filter, smaller particles may also be retained. Colloidal particles that are smaller than the pore size of the membrane filter may attach to the larger particles. Secondly, coagulation may occur in the sample and in the filter, and therefore filtration should be done as quickly as possible after sampling. Thirdly, metals can adsorb onto the filter material and system. (Publication II)

9. Results and discussion

The main results of this study are presented and discussed in Publications I – V. Here a summary of the results is presented. Additional data from ^{222}Rn sampling, quality assurance and the disequilibrium of ^{238}U –series radionuclides in drilled well and dug well water are presented.

9.1 Groundwater sampling

A well-defined sampling strategy should in all cases be developed before the actual sampling takes place. In the sampling of natural radionuclides attention must especially be placed on ^{222}Rn and ^{210}Pb . This is because ^{222}Rn is gaseous in form and easily escapes during sampling, from the sample container during sample transportation and when the sample is prepared in the laboratory. The activity concentration of ^{222}Rn affect that of ^{210}Pb , since ^{222}Rn decays via a chain of several short-lived intermediates to ^{210}Pb . Good guidelines for groundwater sampling are available from the EPA (<http://www.epa.gov/swrust1/cat/pracgw.pdf>, 17.2.2005). ISO standards can also be adapted, but completed standards are not necessarily available for the sampling of natural radionuclides from drinking water (ISO 5667 5, 1991).

9.1.1 ^{222}Rn sampling

The best sample container for ^{222}Rn sampling was a liquid scintillation vial that was pre-filled with liquid scintillation cocktail. The liquid scintillation cocktail traps the ^{222}Rn and thus little of the radionuclide escaped. Another potentially suitable sample container was a glass bottle equipped with a tight cork. The leakage of ^{222}Rn from plastic (polyethylene) bottles was on average $5 \pm 1\%$ per day. An additional 7% total loss was also observed when the container was completely filled and 17% when a small air space was left between the cap and the water surface. In completely filled plastic bottles a part of the ^{222}Rn can diffuse into the polyethylene material, which causes a 7% loss in the activity concentration of ^{222}Rn . In glass bottles where a small air space was left under the cap, approximately 10% of the ^{222}Rn diffused into the air space. This was observed by comparing results for completely-filled and partially-filled glass bottles that were assumed to be ^{222}Rn -tight. For the glass bottles, the additional total loss was not statistically significant. (Publication III)

The difference in activity concentrations between the two parallel ^{222}Rn results was 2%. This was similar to the repeatability of ^{222}Rn determination

(see later). A large amount of ^{222}Rn can be lost when water flows too fast during sampling. This was observed when groundwater samples were collected from the tap using different water flows (Table 5). Using taps at full capacity, the activity concentration of ^{222}Rn was 33% lower than when using a very slow water flow. The loss of ^{222}Rn was due the mixing of air with tap water in the bubble nozzle of the tap.

Table 5. The escape of ^{222}Rn using different water flows. A water flow of 10 – 12 l/min represents the full capacity of the taps (unpublished data).

Water flow (l/min)	^{222}Rn (Bq/l)	The amount of ^{222}Rn escaped (%)
<0.5	1780 ± 90	-
~ 4	1690 ± 85	5
~ 6	1540 ± 80	13
~ 8	1320 ± 65	26
10 – 12	1190 ± 60	33

The median temporal variation in the activity concentration of ^{222}Rn was 17%. Activity concentrations were higher in the samples collected in the summer than in those collected in the winter (Publication I).

9.1.2 ^{210}Pb sampling

Several important factors need to be taken into account in the sampling of ^{210}Pb in ^{222}Rn -bearing drinking water. The transport of a sample from the field to the laboratory normally takes from a few hours to 1–2 days depending on the location of the test site. ^{222}Rn with an activity concentration of 1000 Bq/l produces approximately 0.08 Bq/l of ^{210}Pb during one day. Therefore, ^{222}Rn should be removed from the water immediately after sampling. If this is not done, the time between sampling and ^{222}Rn removal in the laboratory must be known in order to be able to subtract the in-growth of ^{210}Pb activity. This correction can be calculated correctly when the leakage of ^{222}Rn from the sample container is known. The best sample container for ^{210}Pb determination is a glass bottle with a very tight cap, allowing the lowest level of ^{222}Rn leakage, or alternatively a rigid high-quality plastic bottle. More detailed discussion of the leakage of ^{222}Rn and in-growth of ^{210}Pb is presented in Publication III.

There was no clear trend in the temporal variation of the ^{210}Pb activity concentration. The variation was 26% during one day and 33% during several months. Even after excessive water consumption, the activity concentrations of

^{210}Pb were not significantly lower compared to the samples taken directly from the tap before excessive water consumption. (Publications I and II)

9.2 Precision and repeatability

Precision and repeatability for different analytical methods are presented in Table 6. The repeatability of ^{210}Pb analysis was 26%, which was clearly higher than the repeatability with other natural radionuclides. Precision and repeatability improved to 4.9% and 13.6%, respectively, by using different storage containers, acid rinsing and using ^{208}Po as a tracer in the second deposition. The effect of these factors is discussed more in detail in Publication IV.

Table 6. Precision and repeatability of different analytical methods.

Analysed radionuclide	Precision (%)	Repeatability (%)
^{222}Rn	1.6	4.4
^{226}Ra	5.5	15.5
^{238}U and ^{234}U	3.0	8.0
^{210}Pb by Eichrom's method	5.2	14.7
^{210}Pb via ^{210}Po deposition*	9.2	25.6
^{210}Pb via ^{210}Po deposition**	4.9	13.6
^{210}Po	2.0	6.0

* Precision and repeatability calculated from the results which were determinate using ^{209}Po as a tracer in the second ^{210}Po deposition.

** Precision and repeatability calculated from the results which were determinate using ^{208}Po as a tracer in the second ^{210}Po deposition.

Quality management was established in order to ensure reliable results in the laboratory. All methods used in this study are validated. Validation is a process that demonstrates that the results obtained with the used method are reliable, reproducible and that the method is suitable for the particular application (Quevauviller 2002). Additionally, validated methods are documented and the traceability of each result is possible.

Quality assurance of each analytical method includes calibration, internal quality control measurements, analysis of reference materials and participation in proficiency testing or inter-laboratory testing. Participation in inter-comparisons is one of the most important tools to demonstrate analytical quality. Results from in two intercomparison tests for ^{222}Rn , ^{234}U and ^{238}U determinations during 2000 – 2004 are presented in Table 7. The activity concentration of ^{210}Pb in the IAEA-326 sediment sample was analysed as a reference material.

Uncertainty estimations were determined for every analytical method. This comprises the total uncertainty, which includes uncertainty due to weighing

the sample, calibrations, pipetting and uncertainty of the measured activity concentration within 95% confidence limits. Uncertainty due to sampling is not included in the total uncertainty. Uncertainties varied depending on activity level of the sample, since the largest part of the total uncertainty was often caused by activity measurement. Typically, the total uncertainty was 10%, but it varied over a wide range (5 – 50%).

Table 7. Results from two intercomparison tests for ^{222}Rn , ^{234}U and ^{238}U determination during 2000 – 2004. The IAEA-326 sample was analysed as a reference material. Uncertainties in the results are given at the 95% confidence level. The confidence interval was referred to the IAEA certificate.

Code and type of intercomparison	^{222}Rn studied	^{222}Rn reference value	^{210}Pb studied	^{210}Pb confidence interval	^{238}U studied	^{238}U confidence interval
LSC-2001, natural sample Bq/l	$26\,200 \pm 1\,300$	26340	-	-	-	-
IAEA-326, sediment, Bq/kg	-	-	$52.4 \pm 5.0^*$ $54.6 \pm 4.4^{**}$	48.8 - 57.8	-	-
IAEA- 419, synthetic sample Bq/l	-	-	-	-	0.032	0.030 - 0.032
IAEA- 420, synthetic sample, Bq/l	-	-	-	-	0.037	0.035 - 0.037
IAEA- 422, synthetic sample Bq/l	-	-	-	-	0.082	0.082 - 0.084
IAEA- 428, natural sample Bq/l	-	-	-	-	0.059	0.042 - 0.074

* = accredited method, spontaneous deposition of ^{210}Po on a silver disk

** Eichrom's method

9.3 Natural radioactivity in private well water in Finland

Natural radioactivity in Finnish drinking water sources comes mainly from the decay series of ^{238}U . Most of the radioactivity was caused by ^{222}Rn , whereas the activity concentrations of ^{238}U and ^{234}U , ^{210}Po , ^{226}Ra and ^{210}Pb were an order of magnitude lower. Typically, activity concentrations of radionuclides in dug wells were about one tenth of those in drilled wells (Tables 8–9). Higher activity concentrations in bedrock water compared to dug well water were due to the longer contact time of groundwater with soil and bedrock, during which minerals dissolve in the groundwater. Additionally, the mineralogical and geochemical composition of the soil and rock, chemical composition of water, degree of weathering of the rock and redox conditions affect the solubility of radionuclides.

The activity concentrations of ^{222}Rn were log-normally distributed in both drilled wells and wells dug in soil. The activity concentrations of other radionuclides (^{238}U , ^{210}Pb and ^{210}Po) were not as clearly log-normally distributed as ^{222}Rn . In addition, the geometric deviation of ^{238}U , ^{210}Pb and ^{210}Po was larger in different well types. Cumulative frequency distribution plots for ^{222}Rn , ^{238}U , ^{210}Pb and ^{210}Po are presented in Publication I.

Table 8. Statistics on radionuclide activity concentrations in water from drilled wells. The number of samples was 288 (Publication I).

Radionuclide	Mean	Median	Maximum
^{222}Rn (Bq/l)	460	130	8600
^{226}Ra (Bq/l)	0.05	0.01	1.3
^{234}U (Bq/l)	0.35	0.034	12.1
^{238}U (Bq/l)	0.26	0.019	9.9
^{238}U ($\mu\text{g/l}$)	20.9	1.5	800
^{210}Pb (Bq/l)	0.040	0.014	0.54
^{210}Po (Bq/l)	0.048	0.009	2.0

Table 9. Statistics on radionuclide activity concentrations in water from dug wells. The number of samples was 184 (Publication I).

Radionuclide	Mean	Median	Maximum
^{222}Rn (Bq/l)	50	23	710
^{226}Ra (Bq/l)	0.016	0.01	0.06
^{234}U (Bq/l)	0.02	0.004	0.65
^{238}U (Bq/l)	0.015	0.002	0.42
^{238}U ($\mu\text{g/l}$)	1.2	0.18	34
^{210}Pb (Bq/l)	0.013	0.008	0.16
^{210}Po (Bq/l)	0.007	0.005	0.12

The activity concentration of ^{228}Ra in groundwater was not examined in this study. So far, information on ^{228}Ra activities in Finnish drilled well water has been based on 130 measurements in the south of Finland. Thus, ^{228}Ra measurements from the ^{232}Th series have been carried out notably less often than measurements of ^{226}Ra . The highest measured activity concentration of ^{228}Ra has been 0.6 Bq/l, which correspond to an annual effective dose of 0.3 mSv (Asikainen 1982, Kahlos and Asikainen 1973).

9.3.1 Disequilibrium between ^{238}U – series radionuclides

The radioactive secular equilibrium is attained if the system is not interfered with. In equilibrium, the activity concentration of daughter nuclides is equal to the activity of their respective parent. In a state of disequilibrium the ratio between different nuclides differs from one.

Disequilibrium of radionuclides can be characterized by the ratio between different nuclides and between different isotopes. In drilled well water the median activity concentration of ^{222}Rn was thousands of times higher than that of other ^{238}U –series radionuclides. Concerning ^{234}U , ^{238}U , ^{226}Ra , ^{210}Po and ^{210}Pb , most of the radioactivity was caused by ^{234}U and ^{238}U isotopes (U_{tot}). The median ratios of $\text{U}_{\text{tot}}/^{226}\text{Ra}$, $\text{U}_{\text{tot}}/^{210}\text{Pb}$ and $\text{U}_{\text{tot}}/^{210}\text{Po}$ were 5, 4 and 6, respectively. This suggests that ^{234}U and ^{238}U were much more transportable than ^{226}Ra , ^{210}Pb or ^{210}Po . In dug well water, disequilibrium between long-lived radionuclides was not as large as in drilled well water and the median ratios of $\text{U}_{\text{tot}}/^{226}\text{Ra}$, $\text{U}_{\text{tot}}/^{210}\text{Pb}$ and $\text{U}_{\text{tot}}/^{210}\text{Po}$ were 1.2, 1.5 and 2.4, respectively. Disequilibrium between ^{222}Rn and other radionuclides was also not as large as it was in drilled well water. This is probably because ^{222}Rn may escape more easily from dug wells, which are on the average 5 m deep, than from drilled wells. Drilled wells are much deeper than dug wells, on average 60 – 80 m, and they are under tight and often undamaged bedrock. ^{222}Rn may only escape from drilled well water via water flow through the well structure. (Publication I)

In drilled wells, the ratio of $\text{U}_{\text{tot}}/^{226}\text{Ra}$, $\text{U}_{\text{tot}}/^{210}\text{Pb}$ and $\text{U}_{\text{tot}}/^{210}\text{Po}$ varies depending on the activity concentration of ^{222}Rn in water (Table 10). At ^{222}Rn activity concentrations of less than 1000 Bq/l, the ratio of uranium (^{234}U and ^{238}U) to ^{226}Ra , ^{210}Pb and ^{210}Po was between 3 and 6 and no change was observed at different ^{222}Rn levels. At ^{222}Rn activity concentrations higher than 1000 Bq/l, a clearly higher ratio of uranium (^{234}U and ^{238}U) to ^{226}Ra , ^{210}Pb and ^{210}Po was observed. In dug wells, no dependence of the activity concentration of ^{222}Rn on the ratio of $\text{U}_{\text{tot}}/^{226}\text{Ra}$, $\text{U}_{\text{tot}}/^{210}\text{Pb}$ or $\text{U}_{\text{tot}}/^{210}\text{Po}$ was observed. The ratio of $\text{U}_{\text{tot}}/^{226}\text{Ra}$ and $\text{U}_{\text{tot}}/^{210}\text{Pb}$ varied between 1 and 2. However, the ratio of $\text{U}_{\text{tot}}/^{210}\text{Po}$ was higher, between 2 and 4. This shows that the activity concentration of ^{210}Po in dug wells was lower than ^{210}Pb and ^{226}Ra compared to the dissolved activity concentration of ^{238}U and ^{234}U . (Publication I, unpublished data)

The reason for the higher solubility of ^{234}U and ^{238}U compared to ^{226}Ra , ^{210}Po and ^{210}Pb is the chemical composition of Finnish groundwater. The general features of Finnish groundwater are acidity, softness and high Fe- and Mn- concentrations in places (Kujala-Räty et al. 1998). Compared to water in dug wells, bedrock waters are more alkaline, contain more bicarbonate, have a higher alkalinity and change towards the sodium type especially at greater depths (Juntunen 1991, Tarvainen et al. 2001). In such waters, ^{238}U and ^{234}U can form soluble complexes (Langmuir 1978).

Table 10. The median ratios of U_{tot}/Ra , U_{tot}/Pb and U_{tot}/Po in drilled wells at different ^{222}Rn levels in the representative study. (Publication I, unpublished data)

Activity concentration of ^{222}Rn (Bq/l)	Drilled wells			Activity concentration of ^{222}Rn (Bq/l)	Dug wells		
	U/Ra	U/Pb	U/Po		U/Ra	U/Pb	U/Po
All data	5	5	4	All data	1.2	1.5	2.4
<100	3	3	3	<50	1.6	1.4	2.2
100 - 300	6	6	4	50 - 100	1.8	1.7	3.9
300 - 1000	5	5	4	100 - 300	0.9	1.4	1.7
>1000	10	10	9	300 - 1000	1.3	0.6	2.8

The disequilibrium between ^{238}U and ^{234}U isotopes in drilled and dug well water in this study is presented in Figure 7. The mean, median, minimum and maximum $^{234}U/^{238}U$ isotopic ratios in drilled wells were 2.1, 1.8, 0.8 and 10.8 and in wells dug in soil 1.5, 1.3, 0.8 and 4.5, respectively. Figure 7 shows that there was considerable scatter in the concentration and $^{234}U/^{238}U$ activity ratio values for ^{238}U in groundwater, especially in drilled well water, and no clear trend was observed. The largest variation was observed at low uranium concentrations of $<1\mu g/l$. In dug wells, variation in the $^{234}U/^{238}U$ activity ratio was not as large as it was in drilled wells. A similar trend was also observed in dug wells to that in drilled wells. The variation in $^{234}U/^{238}U$ activity ratios was largest at low uranium concentrations of $<1\mu g/l$. (Publication I)

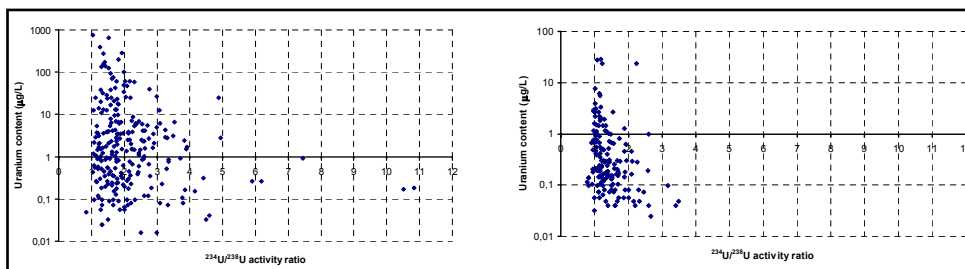


Figure 7. The range of ^{238}U concentrations ($\mu g/l$) and $^{234}U/^{238}U$ activity ratios in water from drilled wells (on the left) and dug wells (on the right). (Publication I, unpublished data)

9.3.2 Correlations between ^{238}U – series radionuclides

Spearman correlation coefficients of radionuclide activity concentrations in water samples from drilled wells and wells dug into soil were calculated and are presented in Publication I. The correlations between various radionuclides were all highly significant in drilled wells ($p < 0.001$). In dug wells the level of significance was not as high. In drilled wells the correlations were around 0.6 and in wells dug in soil around 0.3.

The correlation between ^{222}Rn and ^{238}U was not high ($r = 0.53$ in drilled wells, $r = 0.33$ in wells dug in soil), and correlation between ^{222}Rn and ^{226}Ra was similar to that between ^{222}Rn and ^{238}U . This indicates rather independent behaviour of ^{222}Rn in relation to ^{238}U and ^{226}Ra in groundwater. ^{222}Rn is notably more mobile in groundwater than ^{238}U and ^{226}Ra , whose mobility depends on water quality, unlike that of ^{222}Rn (Tarvainen et al. 2001).

Correlations between ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po were 0.44 – 0.59. The differences in chemical composition of various groundwater samples can be considered the main reason for the rather low correlations. The solubility and mobility of various radionuclides varies according the chemical composition of the water and thus different correlations can be expected. A good example is ^{226}Ra , which is soluble in saline water, whereas the solubility of ^{238}U does not increase with increasing water salinity (Juntunen 1991, Tarvainen et al. 2001).

The correlation between ^{222}Rn and ^{210}Pb was higher than the correlations between ^{222}Rn , ^{238}U and ^{226}Ra . ^{210}Pb enters groundwater two ways: directly by dissolving from the bedrock and by its formation in the water from the decay of ^{222}Rn via short-lived intermediates. Thus, the chemical composition of groundwater has less influence on the occurrence of ^{210}Pb than on the transfer of ^{226}Ra and ^{238}U from the bedrock into groundwater. The slightly lower correlation between ^{222}Rn and ^{210}Po compared to that between ^{222}Rn and ^{210}Pb indicates that ^{210}Po is either adsorbed or precipitated more easily from the groundwater than ^{210}Pb , or that a greater amount of ^{210}Pb is dissolved from the bedrock to groundwater than ^{210}Po .

9.4 ^{234}U , ^{238}U , ^{210}Pb and ^{210}Po removal from drinking water

In order to reduce the dose from drinking water, ^{234}U and ^{238}U removal using an anion exchange resin was examined at six private homes and the removal of ^{210}Pb and ^{210}Po by ion exchange and an activated carbon unit at five private homes. A summary of the results and data on the regeneration of ^{234}U and ^{238}U are presented here. More discussion on the removal of ^{234}U and ^{238}U by strong base anion resins is presented in Publication V and the removal of ^{210}Pb and ^{210}Po by ion exchange and an activated carbon unit in Publication II.

The removal efficiency of ^{234}U and ^{238}U was over 95% at all studied homes, independent of the water quality. The ion exchange units had a high capacity for ^{234}U and ^{238}U . Thousands of bed volumes of natural water can be treated using anion exchange resin without breakthrough. In this study, 6500 BV were treated with the one unit, but this may also be higher. In the later study, it was observed that over 10 000 BV was treated without breakthrough (Vesterbacka et al. 2003). ^{234}U and ^{238}U breakthrough does not primarily limit the use of the unit, but clogging of the unit by accumulating particles or the growth of bacteria inside the unit is more likely. National regulations may also prevent the collection of such amounts of ^{234}U and ^{238}U into the unit. The removal of ^{234}U and ^{238}U from drinking water decreased annual effective doses on average by 0.8 mSv, and at maximum by 1.4 mSv. (Publication V)

Ion exchangers equipped with automatic regeneration can be used for up to 10 years. The removal efficiency of ^{234}U and ^{238}U was close to 100%. Units without regeneration can be used for 2 – 4 years depending on water consumption and raw water quality. The removal efficiency of ^{234}U and ^{238}U in tap units, which are mainly used in summer houses, was dependent on the water flow of the tap. Using taps at full capacity (10–12 l/min), the removal efficiency of ^{234}U and ^{238}U decreased to 80% whereas using a low stream velocity (~ 4 l/min) the removal efficiency was more than 99%. This was due to the short contact time between the water and resin in the unit and therefore not all ^{234}U and ^{238}U was removed from the water. (Publication V)

The water quality of groundwater has no effect on the ^{234}U and ^{238}U removal efficiency, but it must be taken into account while selecting water treatment equipment. High concentrations of iron, manganese and organic matter demand an ion exchanger with automatic regeneration, since these elements are accumulated on the unit and may clog it. Water quality analyses have indicated that water quality was improved. The main water quality improvement in addition to ^{234}U and ^{238}U removal was the removal of organic matter. (Publication V)

Dose rate measurements on the surface of the ^{234}U and ^{238}U removal unit and at various distances from the units showed that the dose rate on the surface of the pure anion exchangers was near the background value, 0.1 – 0.2 $\mu\text{Sv/h}$ (Arvela et al. 1990). This was different from activated carbon units used for ^{222}Rn removal, where the dose rate on the surface may increase to over 100 $\mu\text{Sv/h}$ (Turtiainen et al. 2000a). Exceptions in this study were at test places 1, 3 and 4. At test place 1, the dose rate (11.3 $\mu\text{Sv/h}$) was due to the high activity concentration of ^{222}Rn in raw water (40 000 Bq/l). At test place 3, the dose rate (6.6 $\mu\text{Sv/h}$) was due to the activated carbon unit, which was installed next to the ion exchange unit. At test place 4, the increased dose rate (1.3 $\mu\text{Sv/h}$) was due to ^{226}Ra , which was retained in the unit (removal efficiency 35%) simultaneously with organic matter.

The ion exchange unit more efficiently removed ^{210}Pb and ^{210}Po bound to the small particle fraction than those in the large particle fraction. The removal efficiency varied between 0 – 53% but was in most cases 50%. The efficiency of activated carbon units at removing ^{210}Pb and ^{210}Po was independent of the particle size distribution in groundwater. The removal efficiency varied between 0 – 99% but was in most of the cases higher than 45%. In some cases the activity concentration of ^{210}Pb and ^{210}Po was higher in treated than in untreated (raw) water. This may be a consequence of particles being released from the water treatment equipment into the treated water. Removal efficiencies for stable lead and ^{210}Po by reverse osmosis presented in the literature have ranged from 96 – 98% (Fox and Sorg 1987, USEPA 1991). Compared to this, the removal efficiencies attained by the activated carbon and ion exchange unit in this study were low. (Publication II)

9.4.1 Regeneration of the ion exchange unit

Ion exchange units are usually regenerated 1 – 3 times per week. The main parameters that influence the interval are the amounts of Fe, Mn and organic matter (mainly humus), water hardness, the growth of bacteria and temperature. A saturated salt solution (Na 58 000 mg/l, K 36 mg/l, Mg 69 mg/l and Ca 110 mg/l) was used in the regeneration. The sea salt solution is normally used as a regeneration solution due to its low cost. The amount of salt needed in automatic regeneration was between 3.6 and 8.5 kg depending on the water quality and the size of the ion exchange unit. Regeneration solutions are in most cases drained into the sewer.

The regeneration experiment was carried out at a private home (test place 1, publication V) in order to determine how effectively ^{234}U and ^{238}U can be eluted from the resin with sea salt solution. A flow meter was installed to accurately determine the amount of water consumed during one week (2800 litres). The amount of ^{238}U retained into the ion exchange unit during one week of usage was 2.8 g based on the activity concentrations of raw (1.0 mg/l) and treated water (0.002 mg/l). During the regeneration experiment the salt solutions (385 litres) were collected and the ^{234}U and ^{238}U content was determined in the laboratory by radiochemical analysis (Table 11).

The regeneration started with a counter-current rinse to remove particles and precipitates from the unit. In the counter-current rinse, the increased activity concentrations of ^{234}U and ^{238}U were mainly due to the radioactivity adsorbed onto the particulate matter. The main part of the radioactivity from the unit was removed by a slow wash. During fast washing the salt solution was washed from the unit and it was restored to its original condition. The activity concentrations of ^{234}U and ^{238}U in the treated water also decreased to a very low level.

Table 11. The radionuclide contents in different steps during the regeneration and the corresponding amount of water used in the regeneration study. The pressure during the regeneration procedure varied in the range of 3 – 5 bars.

Step during the regeneration	Water consumed (l)	^{238}U (Bq/l)	^{234}U (Bq/l)
Counter-current rinse	160	13.3	18.1
Salt intake	60	1.3	1.9
Slow wash	60	1768	2422
Fast wash	105	3.4	4.7
Total	385	1786	2447

The combined ^{238}U mass concentration in all regeneration solutions was 2.68g. The regeneration efficiency attained was 96%, but taking into account uncertainties in the results it can be assumed that all ^{234}U and ^{238}U were removed from the resin.

Since the retention of ^{234}U and ^{238}U in the anion exchange resin was not permanent, if the chemical composition of groundwater becomes more saline there is a possibility that ^{234}U and ^{238}U will be released from the resin into the drinking water. Due to this the influence of pH, the pressure in the pipe system and water salinity on ^{234}U and ^{238}U retention in the resin was studied (Vesterbacka et al. 2003). Fifty litres of tap water with low ^{234}U and ^{238}U concentrations (0.003 and 0.002 Bq/l, respectively) were filtered through the ^{234}U and ^{238}U unit with chloride concentrations of 620 mg/l and 1310 mg/l. The results showed that 3.6% and 9.6% of $^{234,238}\text{U}$ was released from the resin, respectively. Changes in pH (from 5 to 10) or pressure (from 2 to 5 bars) in pipe system did not release significant amounts of ^{234}U and ^{238}U from the ion exchange resin.

9.5 Effective doses in Finland

Calculation of the annual effective dose due to ingestion of natural radionuclides in drinking water is presented in Publication I and Chapter 5. The dose from inhalation of ^{222}Rn released from water into indoor air is not taken into account in dose calculations. The mean annual effective dose from natural radionuclides for users of drilled wells was estimated to be 0.4 mSv and for users of wells dug in soil 0.05 mSv (Table 12). The highest dose in this study from all natural radionuclides was 6.8 mSv and from ^{222}Rn 5.5 mSv. Reference values estimated by UNSCEAR (2000) are global age-weighted doses from the ingestion and inhalation of terrestrial radionuclides. The age-weighted effective dose assumes a fractional population distribution of 0.05, 0.3 and 0.65 for infants, children and adults, respectively.

Table 12. Mean, median and maximum annual effective doses (mSv) in this study from different ^{238}U -series radionuclides for users of drilled wells and users of wells dug in soil. The global mean values from ingestion and inhalation of terrestrial radionuclides are presented as reference values (UNSCEAR 2000).

Radio-nuclide	Effective dose, drilled wells (mSv)			Effective dose, wells dug in soil (mSv)			The global mean (mSv)
	Mean	Median	Maximum	Mean	Median	Maximum	
^{222}Rn	0.29	0.08	5.5	0.032	0.015	0.45	0.002 ⁽¹⁾
^{226}Ra	0.010	0.003	0.3	0.003	0.002	0.01	0.008
^{238}U	0.008	0.0007	0.3	0.0005	0.0001	0.01	0.00025
^{234}U	0.014	0.0013	0.5	0.0008	0.0002	0.03	0.00028
^{210}Pb	0.022	0.007	0.3	0.007	0.004	0.08	0.028
^{210}Po	0.046	0.009	1.9	0.007	0.004	0.11	0.085
Total	0.39	0.10	6.8	0.050	0.026	0.60	0.124

¹⁾ Radon released from water into indoor air is not included (0.025 mSv).

The dose estimates in this study were similar to those presented by Mäkeläinen et al. (2002), but differ from earlier reports (Kahlos H. and Asikainen 1980, Salonen 1994). The difference in the dose estimates is due to the data in earlier studies not being representative and due to changes in the dose conversion factors. The most significant changes have been in conversion factors for ^{222}Rn , ^{210}Pb and ^{210}Po . Earlier, the dose conversion factor of 1.0×10^{-8} was used for ^{222}Rn (Kendall et al. 1988). In 1999 a new dose conversion factor of 3.5×10^{-9} was adopted (National Research Council 1999). For ^{210}Po and ^{210}Pb , the dose conversion factors used earlier were 2.1×10^{-7} and 1.2×10^{-6} , respectively and were based on ICRP publication 61. At the present time, they are 1.2×10^{-6} and 6.9×10^{-7} , respectively (ICRP72 1996).

The effective dose arising from ^{222}Rn in drinking water was 75% of the total of all natural radionuclides for users of drilled wells and 60% for users of wells dug in soil (Figure 8). The largest portion of the effective dose from long-lived radionuclides for drilled well users was caused by ^{210}Po . The dose was 12% of the dose caused by all natural radionuclides. For dug well users the largest portion of the effective dose from long-lived radionuclides was caused by ^{210}Po and ^{210}Pb , which both accounted for 13% of the dose caused by all natural radionuclides. The proportion arising from ^{238}U , ^{234}U and ^{226}Ra was very small, only 2 – 6% of the total of all natural radionuclides.

The number of people exposed to different doses is shown in Tables 13 and 14. People exceeding different doses are calculated according to data obtained in this study.

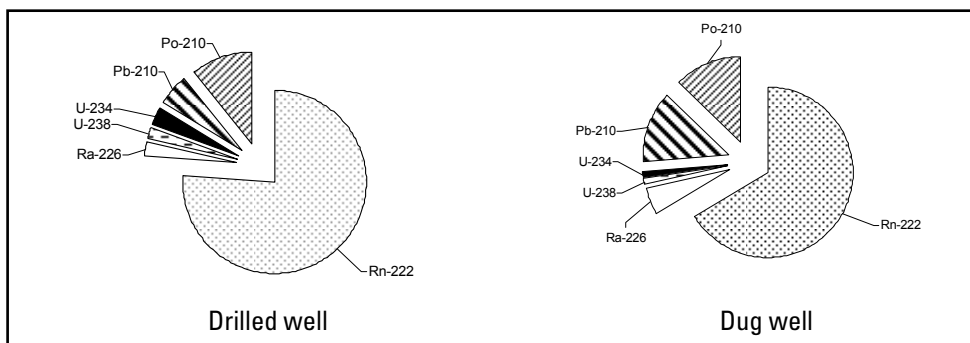


Figure 8. Distribution of the dose from ^{222}Rn , ^{210}Po , ^{210}Pb , ^{234}U , ^{238}U and ^{226}Ra for drilled well users and dug well users (Vesterbacka et al. 2004).

People exposed to high doses, i.e. 0.5 and 1mSv, were users of drilled wells. At all dose levels, the dose was exceeded mainly due to ^{222}Rn . When examining the dose levels of 0.5 and 1mSv, the number of people exceeding the dose levels due to ^{222}Rn was 3 – 4 times higher than the number of people exceeding the dose levels caused by ^{234}U , ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po combined. From among the long-lived radionuclides, all exceeded dose levels were mainly due to ^{210}Pb and ^{210}Po .

High doses for dug well users from natural radionuclides were very rare. The number of dug well users exceeding the dose level of 0.1mSv is only about quarter of the number of drilled well users exceeding the same dose level. The dose caused by ^{234}U , ^{238}U and ^{226}Ra was typically less than 0.05 mSv.

The collective annual doses are presented in Table 15. The highest collective dose is received by people using water from waterworks, totalling about 110 manSv. This is because the number of users is large, even though the activity concentrations of natural radionuclides are low. Private well users receive 46% of the collective annual dose of all Finnish people, and the respective proportion for the users of drilled wells is 39%.

Table 13. Number of people exceeding the doses of 0.05, 0.1, 0.5 and 1 mSv from natural radionuclides in drilled wells according to random sampling (n = 288). The upper limit at the 95% confidence level is presented if there were less than 8 observations. Numbers in parentheses are the precise values observed in this study. ²²²Rn released into indoor air is not taken into account. The number of drilled well users was estimated to be 200 000. (Vesterbacka et al. 2004)

Radionuclide	Number of people				
	Dose less than 0.05 mSv	Dose over 0.05 mSv	Dose over 0.1 mSv	Dose over 0.5 mSv	Dose over 1 mSv
²²² Rn, ²³⁴ U, ²³⁸ U, ²²⁶ Ra, ²¹⁰ Pb and ²¹⁰ Po	50 000	150 000	110 000	37 000	15 000
²²² Rn	72 000	128 000	89 000	30 000	13 000
²³⁴ U, ²³⁸ U, ²²⁶ Ra, ²¹⁰ Pb and ²¹⁰ Po	130 000	70 000	43 000	8 500	less than 7 000 (3000)
²³⁸ U, ²³⁴ U and ²²⁶ Ra	176 000	24 000	15 000	less than 5 000 (2000)	less than 3000 (700)
²¹⁰ Pb and ²¹⁰ Po	150 000	50 000	32 000	less than 7000 (3000)	less than 4000 (1500)

Table 14. Number of people exceeding the doses 0.05, 0.1, 0.5 and 1 mSv from natural radionuclides in dug wells according to random sampling (n = 184). The upper limit at the 95% confidence level is presented if there were less than 8 observations. Numbers in parentheses are the precise values observed in this study. ²²²Rn released into indoor air is not taken into account. The number of dug well users was estimated to be 300 000. (Vesterbacka et al. 2004)

Radionuclide	Number of user				
	Dose less than 0.05 mSv	Dose over 0.05 mSv	Dose over 0.1 mSv	Dose over 0.5 mSv	Dose over 1 mSv
²²² Rn, ²³⁴ U, ²³⁸ U, ²²⁶ Ra, ²¹⁰ Pb and ²¹⁰ Po	220 000	80 000	26 000	less than 8000 (2000)	less than 5000 (0)
²²² Rn	250 000	50 000	20 000	less than 5000 (0)	less than 5000 (0)
²³⁴ U, ²³⁸ U, ²²⁶ Ra, ²¹⁰ Pb and ²¹⁰ Po	280 000	20 000	less than 15 000 (3000)	less than 5000 (0)	less than 5000 (0)
²³⁸ U, ²³⁴ U and ²²⁶ Ra	300 000	less than 5000 (0)	less than 5000 (0)	less than 5000 (0)	less than 5000 (0)
²¹⁰ Pb and ²¹⁰ Po	285 000	15 000	less than 10 000 (3000)	less than 5000 (0)	less than 5000 (0)

Table 15. The collective effective annual doses (manSv) from ^{238}U -series radionuclides for public water user and users of drilled and dug wells.

Water source	Number of users	^{222}Rn (manSv)	^{238}U (manSv)	^{234}U (manSv)	^{226}Ra (manSv)	^{210}Pb (manSv)	^{210}Po (manSv)	Total (manSv)
Drilled well	200 000	58,8	1,7	2,5	2,0	4,0	8,4	77,4
Dug well	300 000	9,6	0,1	0,2	1,0	2,0	1,8	14,7
Water-works	4 700 000	81,0	2,0	3,0	3,0	7,0	12,4	108,4

Table 16. The mean annual effective doses due to exposure to ^{238}U -series radionuclides in drinking water, indoor ^{222}Rn and outdoor gamma radiation in Finland. Reference doses from ingestion and inhalation of terrestrial radionuclides estimated by UNSCEAR, the total annual dose for Finns following the Chernobyl accident, as measured in 1994, are presented.

Source	Mean effective dose (mSv)	Reference
Water from waterworks	0.02	Mäkeläinen et al. 2002
Water from dug wells	0.05	Publication I
Water from drilled well	0.39	Publication I
World wide total age-weighted effective dose from ingested terrestrial radionuclides*	0.14	UNSCEAR 2000
^{222}Rn in indoor air	2	Arvela 1995
Natural gamma radiation	0.45	Arvela 1995
Chernobyl gamma, 1994	0.025	Arvela 1995
Mean annual effective dose to Finns from all sources	3.7	Pöllänen 2003

* From radionuclides ^{238}U , ^{234}U , ^{230}Th , ^{226}Ra , ^{210}Pb , ^{210}Po , ^{232}Th , ^{228}Ra , ^{228}Th and ^{235}U .

The annual effective dose for users of drilled wells from ^{238}U -series radionuclides in drinking water was approximately one tenth of the mean annual effective dose from all sources received by Finns. For users of dug wells and the public water supply the dose from drinking water was 0.05 mSv or less (Table 16). Thus, on average, drinking water causes a minor part of the total dose of Finns. There is, however, a lot of variability in the radionuclide activity concentrations in drinking water depending on the raw water source and the location in Finland. So far, the highest annual effective dose caused by natural radionuclides in drinking water has been as high as 70 mSv (Salonen and Huikuri 2002).

In Finland, the greatest contribution to natural exposure comes from ^{222}Rn in indoor air, which causes the average annual effective dose of 2 mSv. The highest dose from indoor ^{222}Rn has been as high as 350 mSv (Arvela 1995).

UNSCEAR (2000) has estimated that the total age-weighted effective dose from inhalation and ingestion of terrestrial radionuclides is 0.31 mSv, of which 0.17 mSv is from ^{40}K . The rest, 0.14 mSv, is caused by long-lived radionuclides from the ^{235}U , ^{238}U and ^{232}Th series. According to UNSCEAR estimations the main source of exposure comes from the diet. Drinking water accounts for only minor part to the total effective dose.

9.6 Effective doses in Europe

The annual effective doses from ingested water in various European countries are presented in Table 17. Estimates of annual effective doses from natural radionuclides have only been reported from a few countries. Different radionuclides have been included in the dose estimates and comparison of the results is therefore difficult. However, the results indicate that large variation exists in dose estimates.

Effective doses for users of drilled wells have been estimated in Finland, Sweden, Denmark and Ukraine (Isam Salih et al. 2002, Ulbak and Klinder 1984, Zelensky et al. 1993). In all countries, ^{222}Rn caused the largest part of the dose. Generally, effective doses were similar to each other and varied between 0.2 and 0.5 mSv.

The annual effective dose from tap water outside Bornholm to Danish people was estimated to be less than 0.005 mSv (Ulbak and Klinder 1984). In Switzerland, the main dose from drinking water was caused by ^{228}Ra (Deflorin et al. 2004). The median and maximum annual doses caused by ^{238}U , ^{226}Ra and ^{228}Ra were approximately 0.003 and 0.03 mSv, respectively.

In Scotland, Al-Doorie et al. (1993) estimated that the dose from ingested ^{222}Rn from well water was 0.03 mSv, and at maximum 0.05 mSv. In Austria, Schönhofer (1992) estimated that a significant dose from ^{222}Rn from drinking water was caused by the inhalation of ^{222}Rn released from water to indoor air and that the additional effective dose from inhalation of ^{222}Rn was 0.4 – 0.7 mSv. The dose from ingestion of ^{222}Rn was an order of magnitude lower than the dose from inhalation of ^{222}Rn released from water. Ulbak and Klinder (1984) recorded the same kind of observations as Schönhofer (1992) and estimated the annual effective dose due to inhalation of ^{222}Rn released from water to indoor air to be 0.5 mSv.

Table 17. Effective doses from ingested water in different European counties.

Country	Effective dose (mSv)	Radionuclides included in the dose estimation	Reference
Finland	0.39 ⁽¹⁾	^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Po , ^{210}Pb	Publication I
Finland	0.05 ⁽²⁾	^{222}Rn , ^{226}Ra , ^{238}U , ^{234}U , ^{210}Po , ^{210}Pb	Publication I
Sweden	0.51 ⁽¹⁾	^{222}Rn , ^{226}Ra , ^{228}Ra , ^{210}Po , ^{238}U	Isam Salih et al. 2002
Ukraine	0.22 ⁽¹⁾	^{222}Rn , ^{226}Ra , ^{238}U	Zelensky et al. 1993
Denmark	0.16 ⁽⁴⁾	^{222}Rn , ^{226}Ra	Ulbak and Klinder 1984
Denmark	<0.005 ⁽⁵⁾	^{222}Rn , ^{226}Ra	Ulbak and Klinder 1984
Switzerland	0.03 ⁽³⁾	^{238}U , ^{226}Ra , ^{228}Ra	Deflorin et al. 2004
Scotland	0.05 ⁽³⁾	^{222}Rn	Al-Doorie et al. 1993
Austria	0.12 ⁽³⁾	^{226}Ra	Schönhofer 1992
Spain	3.3 ⁽³⁾	^{222}Rn	Galan Lopez et al. 2004
Spain	4.2 ⁽³⁾	Long lived radionuclides	Fernandez et al. 1992
Hungary	<0.1	^{222}Rn , ^{226}Ra	Kovacs et al. 2003
Greece	<0.05	^{222}Rn	Kritidis and Angelou 1984

1) Effective dose for user of drilled wells

2) Effective dose for user of dug wells

3) Maximum effective dose

4) For drilled well users on the island of Bornholm

5) For people living outside Bornholm

In Spain, Galan Lopez et al. (2004) estimated that the annual effective dose from ingested ^{222}Rn varied between 0.0004 and 3.3 mSv. This is similar to the results obtained in this study. Fernandez et al. (1992) estimated that the highest dose from long-lived radionuclides for users of drilled well water comes from radium and for users of dug wells from uranium. This differs from the results obtained in this study, where the highest dose was caused by ^{210}Po .

10. Conclusions

In this countrywide representative study, the mean annual effective dose from natural radionuclides for users of drilled wells was estimated to be 0.4 mSv and for users of wells dug in soil 0.05 mSv. The highest effective dose was caused by ^{222}Rn . The effective dose arising from ^{222}Rn in drinking water was 75% of the total of all natural radionuclides for users of drilled wells and 60% for users of wells dug in soil. In contrast to many other European countries, in Finland the highest contribution to the effective dose from ^{234}U , ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po was caused by ^{210}Po . Only a minor part (8%) of the total dose was caused by ^{234}U , ^{238}U and ^{226}Ra referred from the EU drinking water directive.

The highest activity concentrations of ^{222}Rn , ^{234}U , ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po were found in drilled well water where the median activity concentrations were 1 – 8 times higher than in dug wells. Therefore, the measurement of natural radionuclides in drilled well water is important. From the radiation protection point of view, the most important nuclides to be measured are ^{222}Rn , ^{210}Po and ^{210}Pb . However, measurement of ^{238}U must not be forgotten, even though the dose caused by ^{234}U and ^{238}U is rarely high. In addition to radioactivity, uranium is chemically toxic.

In water from drilled wells the median activity concentration of ^{222}Rn was thousands of times higher than that of other ^{238}U -series radionuclides. From among ^{238}U , ^{234}U , ^{226}Ra , ^{210}Po and ^{210}Pb , the most radioactivity was caused by ^{234}U and ^{238}U isotopes. Their activity concentration in groundwater is high due to their solubility resulting from the chemical characteristics of uranium and the quality of Finnish groundwater. Of the other radionuclides, the highest activity concentrations of ^{226}Ra were found in coastal areas. The activity concentration of ^{226}Ra depends more on the salinity and hardness of the water than on the occurrence of ^{226}Ra , ^{238}U and ^{234}U in bedrock. The most significant correlations observed in this study were between ^{222}Rn and ^{210}Pb and the lowest between ^{238}U and ^{210}Po , both in water from drilled wells and from dug wells.

^{210}Pb and ^{210}Po occur in untreated groundwater as ions, molecules, complexes and bound to particles of different sizes, depending on the chemical composition of the water. The five untreated Finnish groundwaters examined in this study had different size distributions of particle-bound ^{210}Pb and ^{210}Po , but the majority of ^{210}Pb was bound to the large particle fraction (>450nm). By comparison, ^{210}Po was bound more to the intermediate and small particle fraction.

Ion exchange units equipped with a strong base anion resin removed ^{234}U and ^{238}U efficiently from drinking water. The ^{234}U and ^{238}U removal efficiency was

over 95%, independent of water quality. Anion resins have a high capacity for ^{234}U and ^{238}U . Thousands of bed volumes of natural water can be treated without breakthrough. The regeneration efficiency of ^{234}U and ^{238}U with nearly saturated sea salt solution was 100%. Retention of ^{234}U and ^{238}U in the anion exchange resin was not permanent and there is a possibility that at high groundwater mineral concentrations the removal efficiency of ^{234}U and ^{238}U will decline. The removal of ^{234}U and ^{238}U from drinking water reduced the annual effective dose on average by 0.8 mSv and at maximum by 1.4 mSv.

Reliable and efficient removal of ^{210}Po and ^{210}Pb was not achievable using ion exchange or activated carbon units, since they do not completely retain the particles in groundwater to which the radionuclides are bound. The size distribution of particle-bound ^{210}Po and ^{210}Pb varies depending on the chemical composition of the groundwater, which complicates the choice of efficient water treatment. Thus, the only practical method for the efficient removal of ^{210}Po and ^{210}Pb is reverse osmosis.

Quality assurance is important in sampling and radionuclide determination. In sampling, attention must be paid to ^{222}Rn and ^{210}Pb . The best procedure for ^{210}Pb sampling is aeration in the field, which removes ^{222}Rn from the water. If this cannot be done, the sample needs to be collected into a glass bottle with a tight cork that prevents the escape of ^{222}Rn from the sample container in order to correctly subtract the in-growth of ^{210}Pb . For ^{222}Rn , the best container is a small liquid scintillation vial pre-filled with liquid scintillation cocktail. ^{210}Pb determination via ^{210}Po deposition has many sources of error. The main sources of error are adsorption onto the storage container walls, the tracer used in yield determination and the deposition time used in spontaneous deposition, which all need to be taken into account in order to obtain accurate and repeatable results.

Extensive knowledge exists on the activity concentration of ^{238}U -series radionuclides in Finnish groundwater. However, a study on the simultaneous occurrence of natural radionuclides together with other stable elements in groundwater in Finland is needed. The Geological Survey of Finland has examined the regional occurrence of stable elements and correlations between these and radioactive elements, but a study with the main emphasis on radionuclides is lacking. For example, the types of groundwater in which ^{210}Po occurs and the main parameters affecting its occurrence are not known. This could be clarified by multivariate analysis of the simultaneous occurrence of radionuclides together with other stable elements. Moreover, knowledge of the activity concentration of ^{228}Ra from the ^{232}Th series is based on very limited data. More data is needed in order to reliably estimate the effective dose from ^{228}Ra .

In Europe, information is especially lacking on the activity concentrations of ^{210}Pb and ^{210}Po in groundwater. In addition, considerable variation has been recorded in estimates of the effective doses from ingested private well water in various countries. Thus, further investigation of natural radionuclides in groundwater is needed in order to reliably estimate the effective dose caused by these nuclides for the whole EU population

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The natural decay series for ^{235}U , ^{238}U and ^{232}Th

The natural decay series for ^{235}U (Wahl 2000).

Radionuclide	Half-life	α - decay energy (MeV) and intensity (%)	β - decay energy (MeV) and intensity (%)
^{235}U	$7.038 \cdot 10^8 \text{ y}$	4.399 (55), 4.366 (17) 4.215 (5.7), 4.596 (5.0)	-
^{231}Th	25.5 h	-	0.288 (37), 0.305 (35), 0.206 (12.8), 0.287 (12)
^{231}Pa	$3.276 \cdot 10^4 \text{ y}$	5.014 (25.4), 4.951 (22.8), 5.028 (20), 5.059 (11.0), 4.736 (8.4)	
^{227}Ac	21.773 y	-	0.046 (54)
^{227}Th	18.7 d	6.038 (24.2), 5.977 (23.5) 5.757 (20.4)	-
^{223}Ra	11.4 d	5.7162 (52.6), 5.607 (25.7), 5.747 (9.2), 5.540 (9.2)	-
^{219}Rn	3.96 s	6.819 (79.4), 6.553 (12.9), 6.425 (7.5)	-
^{215}Po	1.78 ms	7.386 (100)	-
^{211}Pb	36.1 min	-	1.378 (91.3), 0.525 (6.3)
^{211}Bi	2.14 min	6.623 (83.8), 6.278 (16.2)	-
^{211}Po	4.77 min	-	1.436 (99.7)
^{207}Pb	stable	-	-

The natural decay series for ^{238}U (Wahl 2000).

Radionuclide	Half-life	α - decay energy (MeV) and intensity (%)	β - decay energy (MeV) and intensity (%)
^{238}U	$4.468 \cdot 10^9$ y	4.198 (79.0), 4.151 (20.9)	-
^{234}Th	24.1 d	-	0.199 (70.3), 0.104 (19.2), 0.103 (7.6)
$^{234\text{m}}\text{Pa}$	1.17 min	-	2.290 (98.2), 1.228 (1.0)
^{234}U	$2.455 \cdot 10^5$ y	4.775 (71.4), 4.722 (28.4)	-
^{230}Th	$7.538 \cdot 10^4$ y	4.688 (76.3), 4.621 (23.4)	-
^{226}Ra	1600 y	4.784 (94.4), 4.601 (5.6)	-
^{222}Rn	3.82 d	5.490 (99.9), 4.986 (0.1)	-
^{218}Po	3.11 min	6.002 (100)	-
^{214}Pb	26.8 min	-	0.728 (42.2), 0.67 (48.9), 1.030 (6.3)
^{214}Bi	19.9 min	-	3.275 (18.2), 1.542 (17.8), 1.508 (17.0), 1.425 (8.2), 1.894 (7.4)
^{214}Po	164 μs	7.687 (99.9)	-
^{210}Pb	22.3 y	-	0.017 (80), 0.063 (20)
^{210}Bi	5.0 d	-	1.162 (99)
^{210}Po	138.4 d	5.304 (100)	-
^{206}Pb	stable	-	-

The natural decay series for ^{232}Th (Wahl 2000).

Radionuclide	Half-life	α - decay energy (MeV) and intensity (%)	β - decay energy (MeV) and intensity (%)
^{232}Th	$1.405 \cdot 10^{10}$ y	4.012 (78.2), 3.947 (21.7)	-
^{228}Ra	5.75 y	-	0.039 (40), 0.013 (30)
^{228}Ac	6.15 h	-	1.158 (29.9), 1.731 (11.7), 2.069 (8.6), 0.596 (8.0), 1.004 (5.9), 0.974 (5.1)
^{228}Th	1.913 y	5.423 (72.2), 5.34 (27.2), 5.221 (0.4)	-
^{224}Ra	3.66 d	5.685 (94.9), 5.449 (5.1)	-
^{220}Rn	55.6 s	6.288 (99.9), 5.747 (0.1)	-
^{216}Po	0.145 s	6.778 (99.9)	-
^{212}Pb	10.6 h	-	0.574 (12.3), 0.335 (82.5), 0.159 (5.2)
^{212}Bi	60.6 min	-	2.248 (55.5), 1.521 (4.4)
^{212}Po	0.3 μs	8.785 (100)	-
^{208}Pb	stable	-	-